

INVESTIGATION OF EXPLOSIONS IN IRRADIATED LIQUID-NITROGEN DEWARS

Cards

FACILITY FORM 802

N 66 13092

(ACCESSION NUMBER)

125

(PAGES)

CR 68435

(NASA GR OR TMX OR AD NUMBER)

(THRU)

1

(CODE)

22

(CATEGORY)

Special Nuclear Research
of
National Aeronautics and
Cleveland

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) *\$4.00*

Microfiche (MF) *\$1.00*

ff 653 July 65

NUCLEAR AEROSPACE RESEARCH FACILITY

FZK-219
15 DECEMBER 1964

GENERAL DYNAMICS

NUCLEAR AEROSPACE RESEARCH FACILITY

INVESTIGATION OF EXPLOSIONS IN IRRADIATED LIQUID-NITROGEN DEWARs

J. Romanko

**Prepared for
Space Nuclear Propulsion Office
of the
National Aeronautics and Space Administration
Cleveland, Ohio**

**Contract No. AF 29(601)-6213
Supplement 1**

GENERAL DYNAMICS | FORT WORTH

FOREWORD

The experiments described in this document are designated Task III of the Statement of Work under Supplement 8, Contract AF 29(601)-6213. They were conducted concurrently with the series of tests of NERVA components by the Nuclear Aerospace Research Facility (NARF) of General Dynamics/Fort Worth (GD/FW) for the Space Nuclear Propulsion Office, Cleveland, Ohio (SNPO-C). Results of the first eight tests performed under Contract AF 33(657)-7201 may be found in GD/FW Report FZK-170, Volumes 1 through 8. Subsequent tests are being performed under Supplement 1 of Contract AF 29(601)-6213, with those completed being reported in GD/FW Report FZK-184, Volumes 1 through 4.

AF 29(601)-6213
Task III

ACKNOWLEDGMENTS

The author acknowledges all personnel at NARF who assisted in the work performed under this contract. In particular, E. E. Baggett assisted in the dewar design, and Dr. C. E. Blount and W. J. Green, Jr., assisted with the spectrographic equipment.

The following persons were responsible for the specific experiments indicated below, including written contributions pertaining thereto in this final report:

- . Ray E. Miller (Engineering Experiments);
- . Dr. P. P. Mahendroo, of Texas Christian University, who served as consultant on the EPR work; and P. R. Cheever (EPR Spectroscopy).

ABSTRACT

The studies reported herein were undertaken to investigate the phenomena occurring before, during, and after explosions involving irradiated dewars of liquid nitrogen with various amounts of impurities - including oxygen, water vapor from the ambient air, and solid "catalysts" - in an effort to provide an understanding of the cause of explosions in cryogen test vessels used in nuclear reactor experiments conducted at various laboratories in this country and abroad. The program was divided into two major parts which were run concurrently.

The first part of the program was concerned with experimental studies of an engineering or technological nature to produce explosions under controlled conditions in specially designed open and closed dewars outfitted with various diagnostic instruments and to identify the conditions under which the explosions occur. It was hoped that as a result of the engineering experiments, enough information would be accumulated on the conditions leading to the explosions that it would be possible to initiate explosions under controlled conditions and, hence, to study them by various techniques, including visual, instrumental, and, in particular, spectroscopic techniques. Unfortunately, the program was terminated before sufficient data could be accumulated to attain all of these goals.

The second part of the program involved fundamental experimental studies in the laboratory, using spectrometric instruments,

of the basic phenomena occurring therein to provide an understanding of the fundamental processes that lead to the explosions. In particular, spectrographic studies were conducted in conjunction with the engineering tests, using a common dewar in each experiment, to obtain information on reactions occurring during the explosions. EPR experiments were conducted on samples of irradiated impure LN_2 subsequently investigated for paramagnetic species as a function of irradiation dose, to obtain information on reactions occurring before explosions.

In the engineering experiments and the emission spectroscopy experiments the source of radiation was a nuclear reactor, the Aerospace Shield Test Reactor (ASTR) at General Dynamics/Fort Worth. In the EPR studies the source of radiation was an X-ray unit.

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	iii
ACKNOWLEDGMENTS	iv
ABSTRACT	v
LIST OF FIGURES	ix
LIST OF TABLES	xi
I. INTRODUCTION	1
II. GENERAL EXPERIMENTAL PLAN	6
III. EMISSION SPECTROSCOPY OF EXPLOSIONS IN IRRADIATED LIQUID-NITROGEN DEWARS	8
IV. REACTOR EXPERIMENTS: ENGINEERING EXPERIMENTS AND EMISSION SPECTROSCOPY	14
4.1 Dosimetry	14
4.2 Experiment 1: Open-Dewar Test (9 March 1964)	16
4.2.1 Test-Equipment Description	16
4.2.2 Test Procedure	24
4.2.3 Test Results and Conclusions	28
4.3 Experiment 2: Open-Dewar Test (30 April 1964)	31
4.3.1 Test-Equipment Description	31
4.3.2 Test Procedure	36
4.3.3 Test Results and Conclusions	38
4.4 Experiment 3: Open-Dewar Test (12 and 13 May 1964)	44
4.4.1 Test-Equipment Description	44
4.4.2 Test Procedure	47
4.4.3 Test Results and Conclusions	48
4.5 Experiment 4: Closed-Dewar Test (9 September 1964)	52
4.5.1 Test-Equipment Description	52

TABLE OF CONTENTS (Cont'd)

	<u>Page</u>
4.5.2 Test Procedures	65
4.5.3 Test Results and Conclusions	66
4.6 Experiment 5: Closed-Dewar Test (16 September 1964)	72
4.6.1 Test-Equipment Description	72
4.6.2 Test Procedure	72
4.6.3 Test Results and Conclusions	74
V. EPR SPECTROSCOPY OF IRRADIATED IMPURE LIQUID NITROGEN	81
5.1 Technical Discussion	81
5.1.1 Introduction	81
5.1.2 Paramagnetism of Molecules in Irradiated Impure Liquid Nitrogen	83
5.1.3 Survey of the EPR Studies of O ₂ , O ₃ , NO, and NO ₂	85
5.2 Experimental Program	85
5.2.1 Introduction	85
5.2.2 Resonance Spectra of Expected Paramagnetic Species	86
5.2.3 X-Irradiation of LN ₂ -LOX Solutions	92
5.2.4 EPR Studies: Experiment 4	101
5.3 Conclusions	101
VI. SUMMARY AND CONCLUSIONS	104
6.1 Engineering Experiments	104
6.2 Emission Spectroscopy Studies	107
6.3 EPR Spectroscopy Studies	108
6.4 Concluding Remarks	109
REFERENCES	111
DISTRIBUTION	115

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.	Dosimetry Locations: Open-Dewar Experiments	17
2.	Dosimetry Locations: Closed-Dewar Experiments	18
3.	Open Dewar with Attachments	19
4.	Liquid-Level Probe for Open Dewar	20
5.	Dewar-Pallet Assembly	22
6.	Dewar-Pallet Assembly in the OAT	23
7.	Accessory Equipment: Open-Dewar Experiments	25
8.	Liquid-Level Probe Positions for Open Dewar	26
9.	Experimental Arrangement: Open-Dewar Experiments	27
10.	Spectrograph Setup	29
11.	Spectrograph Housing on OAT Catwalk	30
12.	Deceleration Chamber	33
13.	Test Assembly: Open-Dewar Experiments 2 and 3	34
14.	Close-Up of Top of Test Assembly: Experiment 2	40
15.	Long Shot of Test Assembly: Experiment 2	41
16.	Baffle Plate after Experiment 2	43
17.	Modified Liquid-Level Probe Positions for Open Dewar	45
18.	Closed Dewar with Fittings and Window	53
19.	Disassembled Closed Dewar	54
20.	Schematic of Closed Dewar	55
21.	Accessory Equipment in OAT Area: Closed- Dewar Experiments	59

LIST OF FIGURES (Cont'd)

<u>Figure</u>		<u>Page</u>
22.	Experimental Arrangement: Closed-Dewar Experiments	61
23.	Accessory Equipment: Closed-Dewar Experiments	63
24.	Resistor and Thermocouple Positions: Closed-Dewar Experiments	64
25.	Cryogen-Chamber Liquid Temperature vs Actual Test Time: Experiment 4	69
26.	Cryogen Liquid-Mixture Temperature vs Liquid Oxygen by Volume: Laboratory Experiment	73
27.	Cryogen-Chamber Liquid Temperature vs Actual Test Time: Experiment 5	77
28.	Cryogen Boil-Off Rate: Experiment 5	80
29.	EPR Spectrum (First Derivative) of NO ₂ in LN ₂	88
30.	EPR Spectrum (First Derivative) of NO ₂ in LN ₂ : Rotated Sample	90
31.	Supply Dewar Assembly	95
32.	EPR Spectrometer and X-Ray Unit	96
33.	Spectrometer Magnet with X-Ray Tube Removed	97
34.	Spectrometer Cavity and Quartz Dewar	98
35.	EPR Spectrum (First Derivative) of Quartz Sample Dewar	100
36.	EPR Spectrum (First Derivative) of Fused-Quartz Window	102

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1.	Dosimetry Data: LN_2 Irradiations	15
2.	Calculated Temperatures from Rubicon Data: Experiment 4	68
3.	Calculated Temperatures from Rubicon Data: Experiment 5	76
4.	Melting and Boiling Point Temperatures	87

I. INTRODUCTION

The systematic testing of NERVA materials, components, and systems intended for application at cryogenic temperatures in a nuclear reactor environment has met with some problems, especially evinced in explosions which have occurred in cryogenic test chambers employing liquid nitrogen as the cryogenic fluid. In an effort to obtain information on the nature of these explosions, a fairly comprehensive survey of the literature was conducted by this author prior to the start of the studies performed herein. This survey appears in Reference 1 ("Technical Discussion") as introductory material to the main technical proposal on studies of explosions in irradiated LN_2 vessels and will not be repeated here; it covers some 20 references (Refs. 2-21).

This literature on irradiated cryogenic vessels employing liquid nitrogen as the cryogen revealed a number of conflicting observations and conclusions. That these apparent discrepancies in results have occurred is not too surprising in view of the varied nature of the experiments conducted; the configurations were selected mainly from the point of view of obviating explosions rather than of trying to understand their nature. Furthermore, the experiments involved dewars designed to cool extremely small samples, such as high-purity-metal single crystals and semiconductor materials used in fundamental studies of radiation effects thereto, so that the actual dewar volumes were extremely

small, generally less than one liter. Also, reactors of relatively low gamma fluxes were employed so that flow rates and, hence, amount of cryogen used were small. In some experiments in connection with the NERVA program, however, large experimental arrangements have been used (up to 20 gal in capacity) in which large flow rates of liquid nitrogen have been employed (up to 30 gal per hour) indicative of the large amount of nuclear heating attending high gamma flux ($\sim 10^8$ r/hr) reactors.

Data on the radiation chemistry of irradiated nitrogen with small amounts of oxygen as the main impurity is virtually nonexistent. Furthermore, that information which does exist on the radiation chemistry of irradiated mixtures of liquid oxygen and nitrogen - and of irradiated liquid oxygen - is of little assistance in describing the processes leading to explosions in irradiated impure liquid nitrogen.

A review of accident reports and brief descriptions in the literature revealed that the explosions have occurred during warmup periods after the liquid nitrogen had evaporated and, apparently, when the ambient had been admitted to the vessel. In some cases, the explosions occurred within a few hours; in other cases, a day or two after reactor shutdown. It has been suggested that the explosions are caused by ozone, formed from traces of oxygen in the nitrogen, which is explosive under the circumstances of the accidents. Others claim that ozone is not formed under these circumstances, but that oxides

of nitrogen are formed which lead to the explosions. It is concluded that the information available is of questionable accuracy and significance; but to the extent that it permits conclusion, it indicates that the main product may be ozone or oxides of nitrogen, that these products may decompose explosively, and that their explosion is probably initiated by the ambient.

Although it should thus be possible to avoid explosions by using small quantities of high-purity-grade nitrogen and by preventing the ambient from getting into the system, these measures can only reduce, but not eliminate, the hazard, because these measures are made ineffective if the system springs a leak to the ambient. Complete elimination of the explosion hazard can only be achieved by suppressing the formation of the explosive product, even if oxygen is present and the ambient is admitted. This could conceivably be accomplished by introducing a suitable inhibitor into the system.

None of the explosions reported in the literature has caused injuries to personnel or serious damage to equipment. This fortunate outcome is attributable to the special circumstances and procedures of testing and should not be construed to indicate that the explosions are inherently harmless. Thus the explosions have occurred after shutdown of the reactor and after removal of the test vessel from the reactor and when operating personnel have been at a radiation-safe distance from the vessel. Serious accidents may well occur under less favorable conditions.

As already pointed out, the information available is insufficient for the identification of the necessary and sufficient conditions for explosion. Not even the explosive material can be identified with certainty. In this position, safety precautions will be based upon conjecture rather than upon understanding and experience. Furthermore, dewar vessels designed on the basis of the available data cannot be considered explosion-proof with any reasonable degree of certainty.

It was felt that to eliminate - not simply to obviate - the explosion hazard, a specific program should be conducted for NASA/AEC on studies of explosions in irradiated liquid-nitrogen vessels. This feeling came from a consideration of (1) the extent of the NERVA testing programs employing liquid-nitrogen dewars currently underway at the Nuclear Aerospace Research Facility (NARF) at General Dynamics/Fort Worth (GD/FW), (2) the added emphasis on experimental and ground-based tests for the NERVA program in general since the cancelation of the RIFT program, and (3) the possibility of conducting irradiation tests at liquid-nitrogen temperatures at NASA's Plum Brook Reactor Facility at Sandusky, Ohio, and at the ETS 1 and ETS 2 facilities at Jackass Flats, Nevada (with a NERVA engine as the reactor source inside the 30-ft.-diam biological shield).

The studies reported herein were designed to obtain the information required for the identification of the necessary

and sufficient conditions for explosions in irradiated liquid-nitrogen vessels and for the understanding of the processes and the phenomena involved. The ultimate aim was to eliminate the explosion hazard, not simply to obviate it. Unfortunately, this program was terminated prematurely, so that the information summarized in this report is somewhat incomplete in its contribution to the understanding of the explosion mechanisms.

II. GENERAL EXPERIMENTAL PLAN

This study was undertaken to investigate the phenomena occurring before, during, and after explosions involving irradiated dewars of liquid nitrogen with various amounts of impurities - including oxygen, water vapor from the ambient air, and solid "catalysts" - in an effort to understand the cause of explosions in cryogen test vessels used in nuclear reactor experiments (Ref. 1). The program was divided into two major parts, run concurrently. The first concerned experimental studies of an engineering or technological nature to produce explosions under controlled conditions and to identify the conditions under which they occur. The second part involved fundamental experimental studies in the laboratory of the basic phenomena occurring therein to gain an understanding of the fundamental processes leading to cryogenic test-vessel explosions.

NARF personnel designed engineering experiments first to learn how to produce explosions under controlled conditions and thence, by studying these explosions with various means of observation, to determine whether the onset of explosions require the following conditions: complete evaporation of the liquid nitrogen; a temperature rise above that of liquid nitrogen; admission of the ambient air and, if so, what constituent of the ambient air is effective in initiating explosion; the catalytic effect of metals and/or organics in contact with the liquid nitrogen; and whether metal catalysts used

for the deactivation of active nitrogen act as inhibitors of explosions. In all of the engineering experiments, the source of radiation was the ASTR.

It was hoped that as a result of these engineering experiments, enough information would be accumulated on conditions leading to explosions so that it would be possible to initiate explosions under controlled conditions and thence to study them by various techniques. These would include visual and instrumental techniques and, in particular, such spectroscopic techniques as emission spectrography and electron paramagnetic resonance (EPR) spectrometry. Unfortunately the program was terminated before sufficient data could be accumulated to attain all of these goals.

The fundamental studies undertaken in this program were directed towards identifying the products formed in the irradiated liquid nitrogen and towards studying their reactions insofar as they contributed to the explosions. Various sources of radiation were used in these fundamental studies, including neutrons and gamma rays from a nuclear reactor, the ASTR, and X-rays from a radiographic source.

The spectrographic studies were conducted with the dewars used in the engineering tests described above. The EPR experiments were conducted with samples irradiated with X-rays in situ in the microwave cavity and subsequently investigated for paramagnetic species.

III. EMISSION SPECTROSCOPY OF EXPLOSIONS IN IRRADIATED LIQUID-NITROGEN DEWARS

Studies of the characteristics of optical radiation emitted by luminous bodies have been instrumental in determining the physical and chemical conditions of the emitting species in the auroras of the night sky, luminous tails of comets, stellar atmospheres - to mention only a few examples.

Spectroscopic investigations of band spectra appearing in electric discharges in gases, in flames, and in explosions can yield quantitative information on the concentration of the emitting species if the condition of excitation is established. Information can also be obtained on the individual steps of a given chemical reaction and, particularly, of the chemiluminescence accompanying them, such as in the combustion of H_2 in air. Heats of elementary reactions, which are not otherwise accessible to direct measurement, can be calculated accurately from heats of dissociation of the molecules involved, the latter being obtainable from spectroscopic techniques. Band spectroscopy can be used to study not only the elementary processes in chemical reactions, but also the equilibria of chemical reactions in gases on the basis of spectroscopic data obtained therefrom (Ref. 22).

The emission spectroscopy studies planned in the current program were undertaken to provide information on the concentration of the emitting species and of the types and strengths

of the chemical reactions occurring in detonations in dewar vessels of irradiated liquid nitrogen containing various impurities, including oxygen and water vapor. In the follow-on studies proposed to this task, investigations with a framing and streaking camera used with the spectrograph would yield information on the temporal and spatial changes of the spectra emitted therefrom. Used without the spectrograph, the framing camera would yield information on the temporal and spatial changes of the explosions occurring within the irradiated dewar.

The spectra of the emitting species in the explosive flashes should include the molecular bands of N_2 (first positive and second positive systems); N_2^+ (first negative system); NO (β and γ systems); O_2 (Schumann-Runge system); and O_3 systems, among others.

The emission of the first positive bands of molecular nitrogen have been used to measure the recombination rate of atomic nitrogen in 3-body reactions (Ref. 23). Since the emission of the nitric-oxide β bands is proportional to the product of the atomic-nitrogen density and the atomic-oxygen density - whereas the intensity of the first positive bands is proportional to the square of the nitrogen atom density - the ratio of the β bands to the first positive bands gives the ratio of the number of oxygen atoms to the number of nitrogen atoms. The simultaneous observation of these two emissions permits the measurement of the 3-body recombination of atomic

nitrogen to form molecular nitrogen; atomic nitrogen, atomic nitrogen, and oxygen to form nitric oxide; and atomic oxygen to form molecular oxygen (Ref. 24). The reaction between nitric oxide and atomic oxygen, which produces a green afterglow, has been used to measure both the rate of the nitric-oxide-atomic-oxygen 3-body reaction (Ref. 25) and the 3-body atomic-oxygen reaction (Ref. 26). Thus measurements of the relative intensities of various band systems in the explosive flashes should yield information of the physical and chemical conditions therein, including a measure of the kinds and relative amounts of various emitting species (Ref. 27).

Because the flashes of light attending the explosions in irradiated LN_2 dewars are of extremely short duration and the intensity of the flashes is low, these studies required the use of a high-speed spectrograph to record the luminous events. Furthermore, the spectrograph selected must display sufficient dispersion (and resolution) for an adequate analysis of the spectral lines and band structures. Hence, a Jarrell-Ash Model 75-000 high-speed, large-aperture, plane-grating spectrograph with $f/\text{No.}$ of $f/6.3$, used in shock tube luminescence studies, was employed in these investigations. The size of the dewar test vessels utilized in these studies was optimized so that the field of view therein, when matched with the appropriate condensing lens, filled the collimator lens of the basic $f/6.3$ instrument.

The choice of this instrument was based also on a number of other desirable features required in these investigations. At the optimum position, the f/6.3 spectrograph, with a 300-groove/mm plane grating, will resolve lines that have a density of 1.0 and are 0.8 Å apart at dispersion of 42 Å/mm; the resolution drops to 1.6 Å at a density of 2.0 and, at the extreme edge of the 5-in. field, the resolution is 1.8 Å at $d = 1.00$ and 4.6 Å at $d = 2.0$. These characteristics compare favorably with those of the f/10 and f/4 instruments which were used by Bass and Broida in the free-radical studies in solid N₂, O₂, and H₂ at the National Bureau of Standards (Ref. 28). With the f/10 instrument they resolved 1.5 Å at 5200 Å (using glass optics) and 0.5 Å at 2600 Å (using quartz optics); with the f/4 instrument they resolved 4 Å at 5200 Å (glass optics) and 0.8 Å at 2600 Å (quartz optics).

The large wavelength coverage of the f/6.3 spectrograph was also desirable in these studies, being from 2000 Å to 20,000 Å, with approximately 5400 Å wavelength coverage (first order spectrum) in one exposure (5-in. plate). Thus in one exposure, it would be possible to cover the range from 2000 Å to 7400 Å - which would be sufficient to record most of the emission spectra arising in the exposure due to the species of interest in this study.

In some of the early experiments - in particular, those involving the open dewars - a low-dispersion, high-aperture instrument, the f/6.4 A-O Spencer spectroscope outfitted with

an Edmund Scientific Company reflection replica grating and a Polaroid camera attachment was employed. This setup was used strictly to determine the level of intensity of the flashes of light accompanying the explosions prior to use of the high-dispersion equipment. Some difficulties were experienced in utilizing this setup, however, in view of its make-shift nature; for, during extended exposure periods, the intensity of the stray light as recorded by the fast film was too great to warrant its use in recording weak flashes of short duration.

Matching of the source of radiation (in the dewar) with either spectrograph was accomplished by the use of a Bausch and Lomb achromatic condensing lens (focal length of 240.9 mm and diameter of 63.0 mm) and an aluminized-front surface-reflecting mirror mounted on a common stand.

A number of different types of emulsions were available in this study, including Eastman Panatomic-X (ASA 16), Eastman Kodak 103 a0, Eastman Kodak Tri-X, and Polaroid ASA 300 and ASA 10,000 films. The types of emulsion used during the exposure periods in waiting for the explosions depended upon a number of considerations, including length of exposure (wait) time, level of background radioactivity, level of background stray light (in the open-dewar experiments in which a "light pipe" was not used), and relative humidity and temperature (when using Polaroid films), among other factors.

To aid in the analyses of the spectral lines and band

structures for identification and concentration of the emitting species, the available accessory equipment were a JACO densitometer for the measurement of line and band intensities and a traveling microscope for the measurement of spectral lines and band frequencies. Use would also be made in the analysis of the extensive literature on emission spectroscopy of free radicals in the solid (and liquid) phases of oxygen, ozone, nitrogen, and oxides of nitrogen, as compiled by Bass and Broida of the National Bureau of Standards (Ref. 28). To aid in the positive identification of the observed spectral lines, reference spectra of some of the above constituents were obtained in the laboratory with the appropriate discharge (Plücker) tubes. The "standard" iron arc spectrum and/or low-pressure mercury arc spectrum would serve as the calibration spectra.

Since the "engineering experiments" and the spectrographic studies using the ASTR as the irradiation source were run concurrently, the two experiments have been combined in this report. Thus the descriptions of the experimental procedures used in the spectrographic studies - including setup and alignment of the equipment on the OAT catwalk after reactor shutdown, and attempts to record emission spectra during boil-off of the liquid nitrogen in the irradiated dewars - are included with those on the "engineering tests" in Section 4.

IV. REACTOR EXPERIMENTS: ENGINEERING EXPERIMENTS AND EMISSION SPECTROSCOPY

An account is given herein of the five experiments conducted on explosions in irradiated dewars of liquid nitrogen containing various impurities, including oxygen and water of the ambient air. The first three experiments involved "open" dewars: open-mouth commercial stainless-steel dewars outfitted with various accessories. The last two experiments involved "closed" dewars: specially constructed stainless-steel dewars with lids to exclude the ambient air, but outfitted with supply tubes, vent tubes, and diagnostic instruments and permitting observation therein through fused-quartz windows with a telescope, TV camera, and spectrograph.

Accounts of the experiments, including test-equipment description, test procedure, and test results, are given chronologically for each of the five irradiation runs, numbered 1 through 5.

4.1 Dosimetry

Table 1 records the exposure levels of radiation in the vicinity of the dewars as measured with nitrous-oxide dosimeters for the gamma-ray exposure doses; sulfur pellets and aluminum foils for the integrated neutron fluxes beyond 2.9 Mev and 8.1 Mev, respectively (that is, the so-called fast flux); and gold foil data (with and without cadmium covers) for the

Table 1

DOSIMETRY DATA: LN_2 IRRADIATIONS

Experiment No.	Experiment Date	Dosimeter Location†	nvt _{th} (n/cm ²)	nvt > 2.9 Mev (n/cm ²)	nvt > 8.1 Mev (n/cm ²)	γt (r)
1	3-9-64	Front (A) Back (B)	2.42 {15}* 3.01 {14}	7.38 {14} 9.14 {13}	3.16 {13} 3.88 {12}	1.15 {8} 1.73 {7}
2	4-30-64	Front (A) Back (B)	1.21 {15} 2.87 {14}	8.75 {14} 9.85 {13}	3.30 {13} 3.81 {12}	1.23 {8} 1.21 {7}
3	5-12-64 5-13-64	Front (A) Back (B)	3.20 {15} 3.11 {14}	8.64 {14} 1.00 {14}	1.72 {13} 2.20 {12}	1.15 {8} 1.64 {7}
4	9-9-64	Front (A') Back (B')	1.01 {14} 1.20 {14}	2.30 {15} 2.28 {14}	5.78 {13} 7.29 {12}	1.45 {8} 1.21 {6}
5	9-16-64	Front (A') Back (B')	2.72 {13} 1.70 {14}	3.11 {15} 2.86 {14}	9.20 {13} 9.21 {12}	1.45 {8} 2.19 {7}

* (n) = 10^n

† Refer to Figures 1 and 2

integrated thermal-neutron fluxes. The positions of the dosimetry packets are shown in Figures 1 and 2. These centerline dosimetry data on the front and back faces of the dewar-pallet assembly in each experiment bracket the level of irradiation expected inside the dewar. No attempt is made to explain the few anomalies in these data nor to determine accurately the levels of irradiation inside the dewars, since no quantitative results are forthcoming in this series of reactor experiments.

4.2 Experiment 1: Open-Dewar Test (9 March 1964)

4.2.1 Test-Equipment Description

Experiment 1 was the first of a series of three "open-mouth" dewar tests. The dewar used in each case was a stainless-steel Hofman E2 with an inside diameter of 6 in., an inside depth of 18 in., and a capacity of 8.12 liters. The dewar was fitted with a bracket upon which a liquid-level probe and a liquid-nitrogen fill line could be attached (Fig. 3).

The liquid level probe was constructed with a stainless-steel fitting and tube containing seven copper-constantan thermocouples and four 1000-ohm carbon resistors placed at various intervals along the probe (Fig. 4). The thermocouples were made from 24-gage wire insulated with Fiberglas and secured to each other and to the probe with glass string. The thermocouple junctions were formed by fusing the wires with a torch.

To provide safe confinement of the dewar during and after the irradiation and proper alignment of the dewar with the

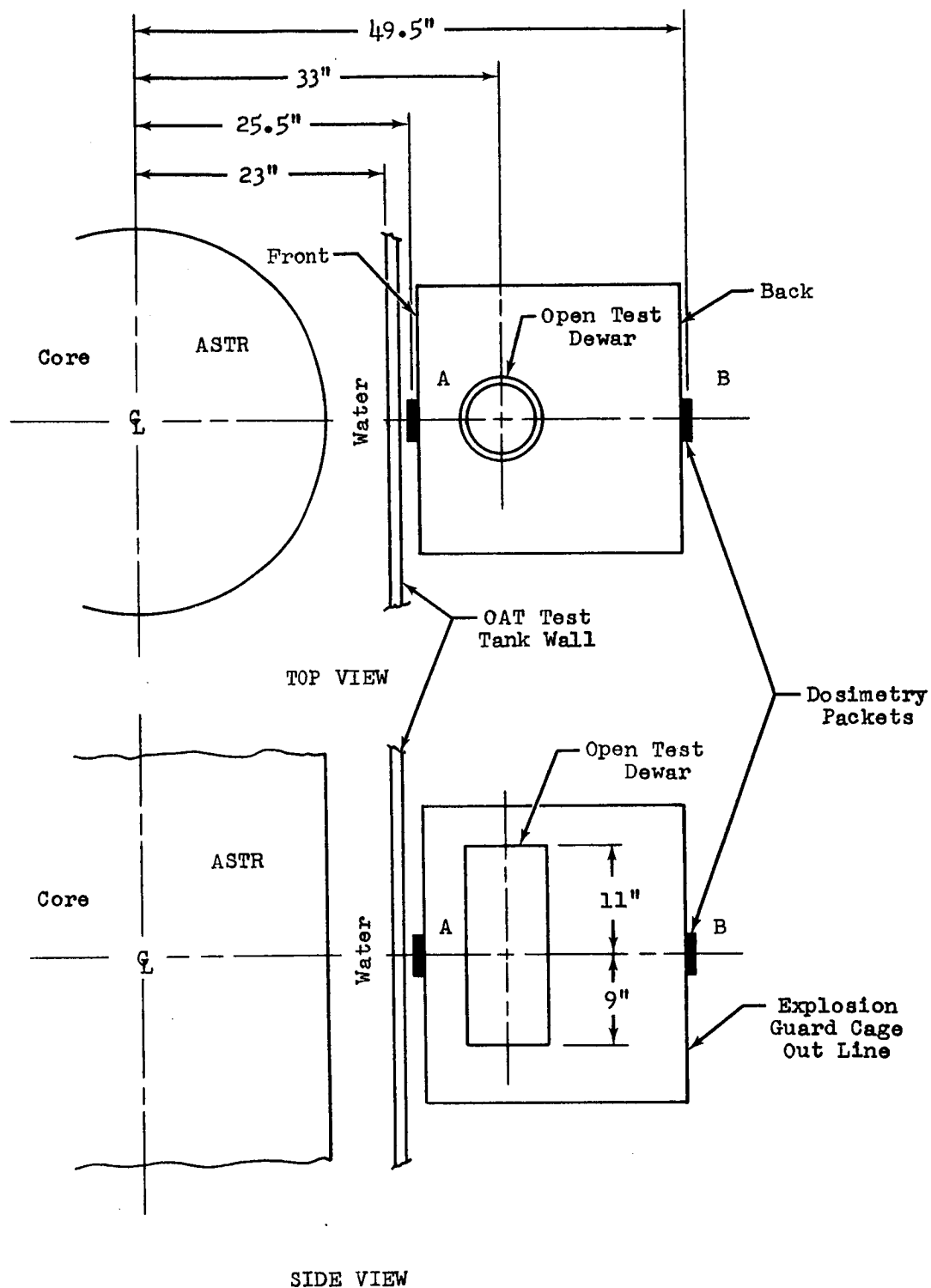


Figure 1 Dosimetry Locations: Open-Dewar Experiments

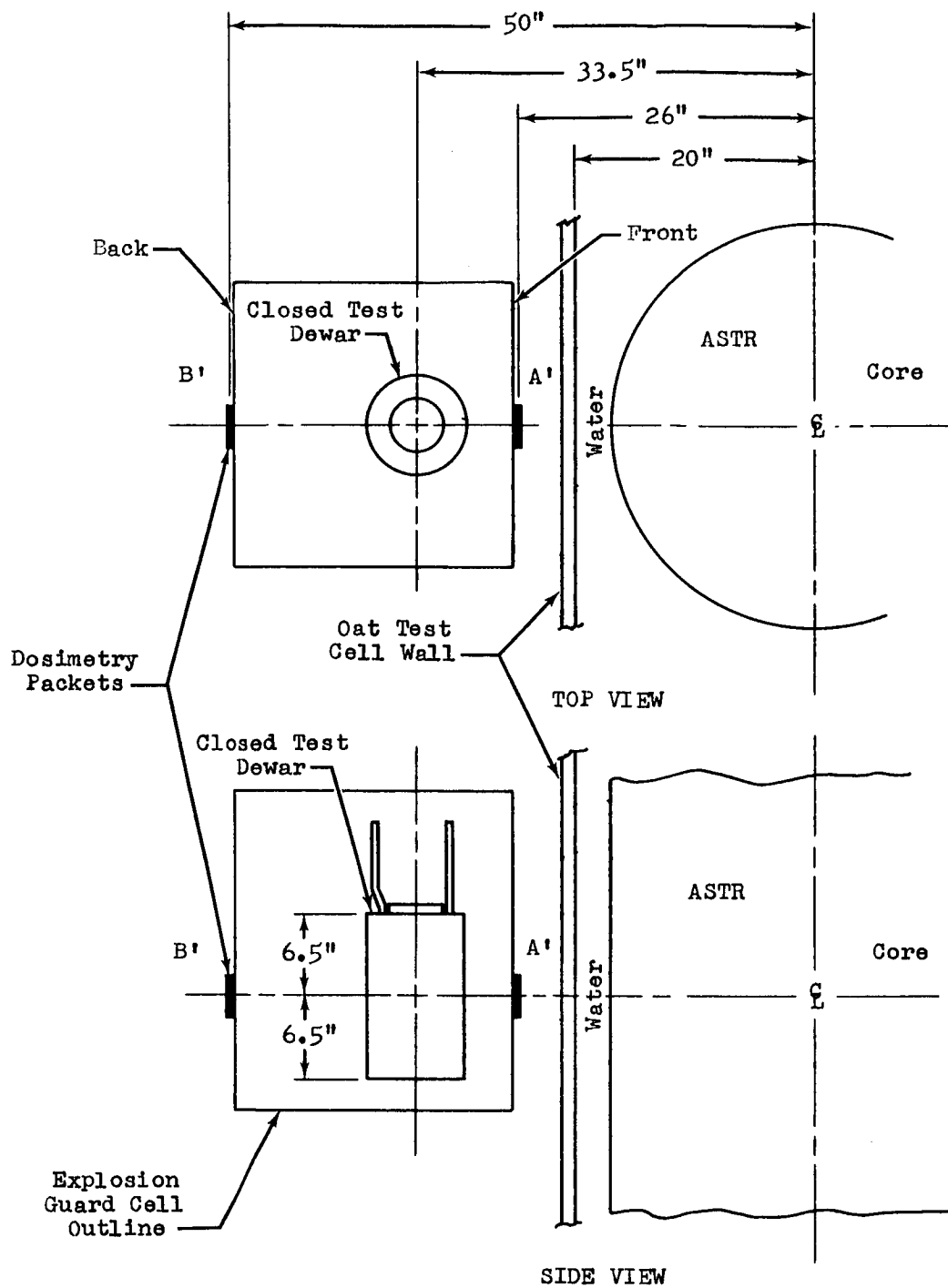


Figure 2 Dosimetry Locations: Closed-Dewar Experiments

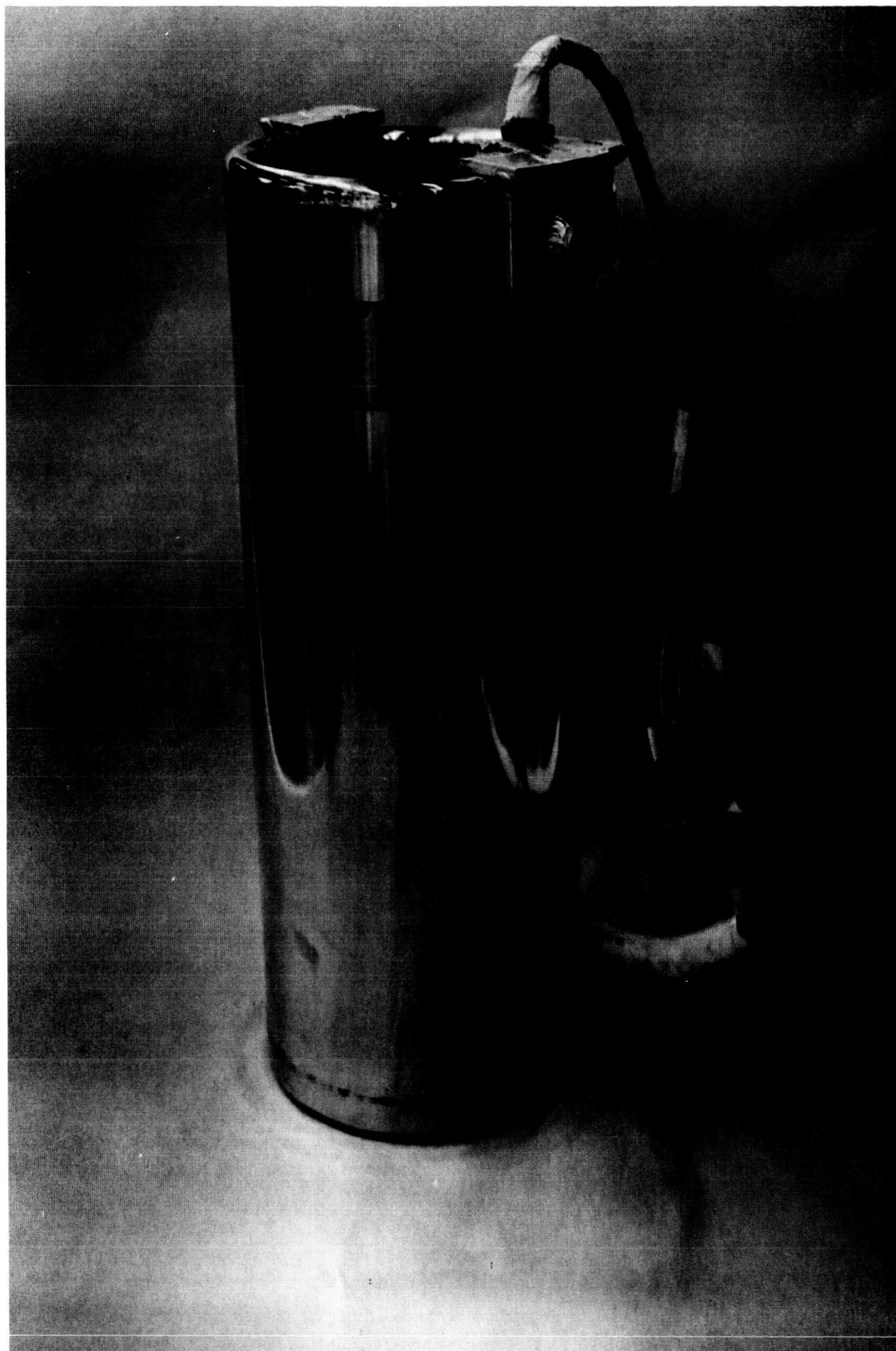


Figure 3 Open Dewar with Attachments

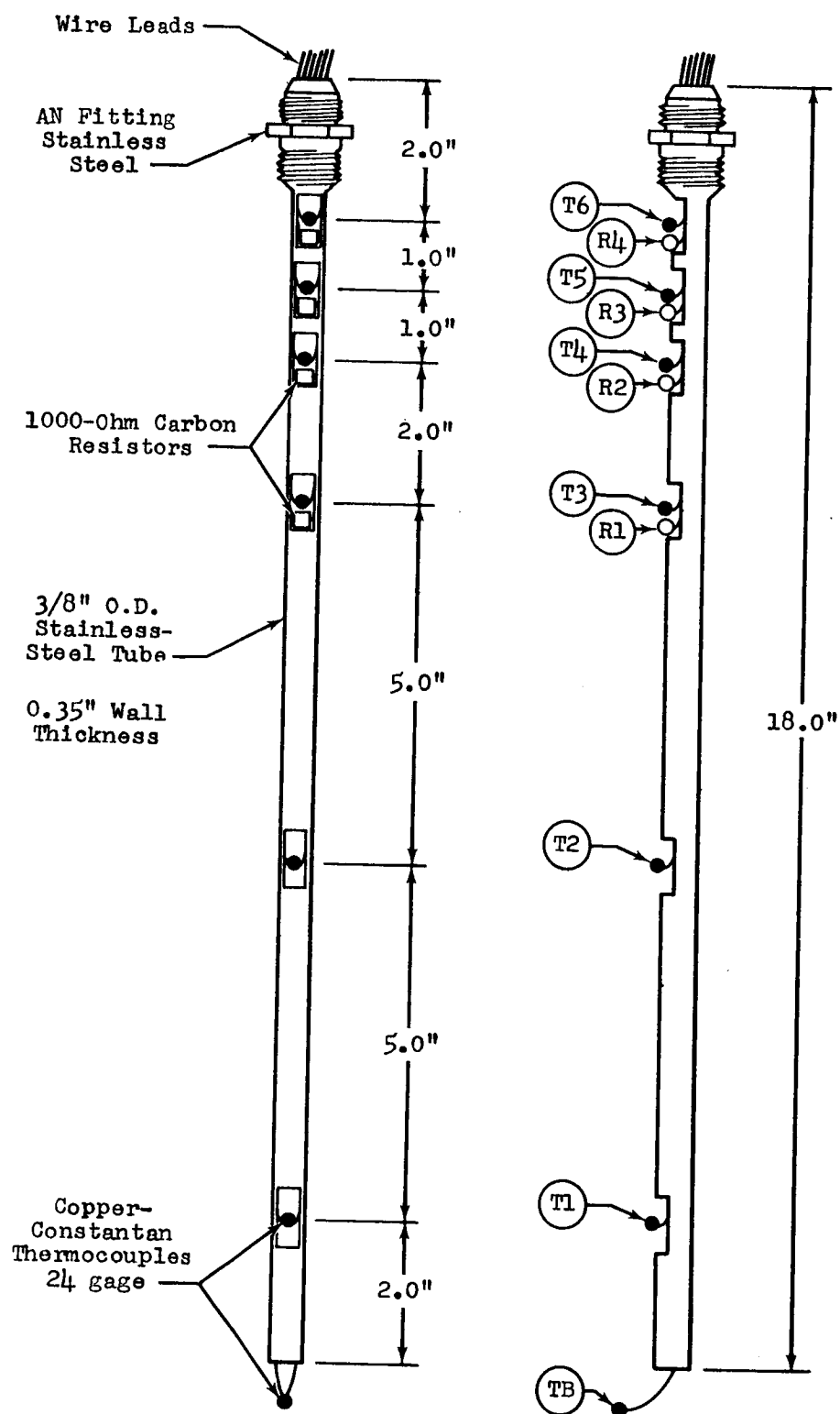


Figure 4 Liquid-Level Probe for Open Dewar

spectrograph and associated equipment, a special aluminum frame (pallet assembly) was constructed, including a cage with the sides consisting of an aluminum explosion-guard screen inside which the dewar was housed (Fig. 5). A hole 6 in. in diameter was cut in the top screen of the explosion-guard cage at a point directly above the open mouth of the installed dewar to provide for viewing the inside of the dewar with the telescope and spectrograph.

The spectrograph employed in the open-dewar experiments was the low dispersion $f/6.4$ A-O Spencer spectroscope outfitted with an Edmund Scientific reflection grating and a polaroid camera attachment. An achromatic condensing lens (Bausch and Lomb, focal length of 240.9 mm and diameter of 63.0 mm) and a front-surface reflecting mirror were used to match the source (dewar) and the spectrograph. To facilitate the setup and alignment of the optics (mirror, condensing lens, and spectrograph) during pre- and post-irradiation checkout, a 40-w incandescent light held by a stand was placed on top of the screen near the hole and moved to a position directly over the mouth of the dewar until the checkout was complete (Fig. 6).

A 500-gal liquid-nitrogen storage tank containing a pure grade of LN_2 (<20 ppm O_2) was placed near the Outside ASTRO Tank (OAT) as the supply source for the dewar during the experiment. An Armaflex-insulated 1/2-in. copper line was connected from the 500-gal tank to a pneumatic-operated variable-control

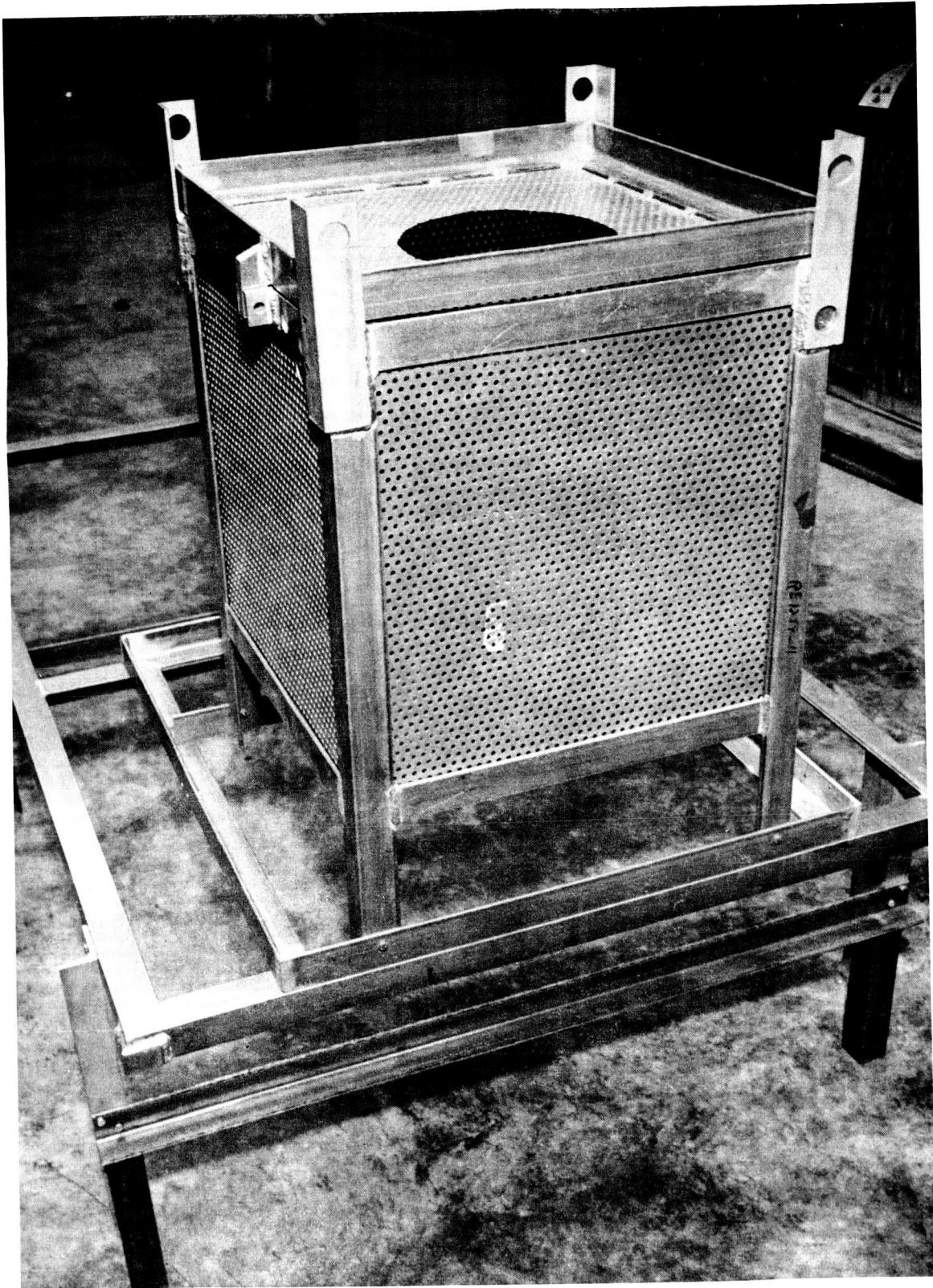


Figure 5 Dewar-Pallet Assembly

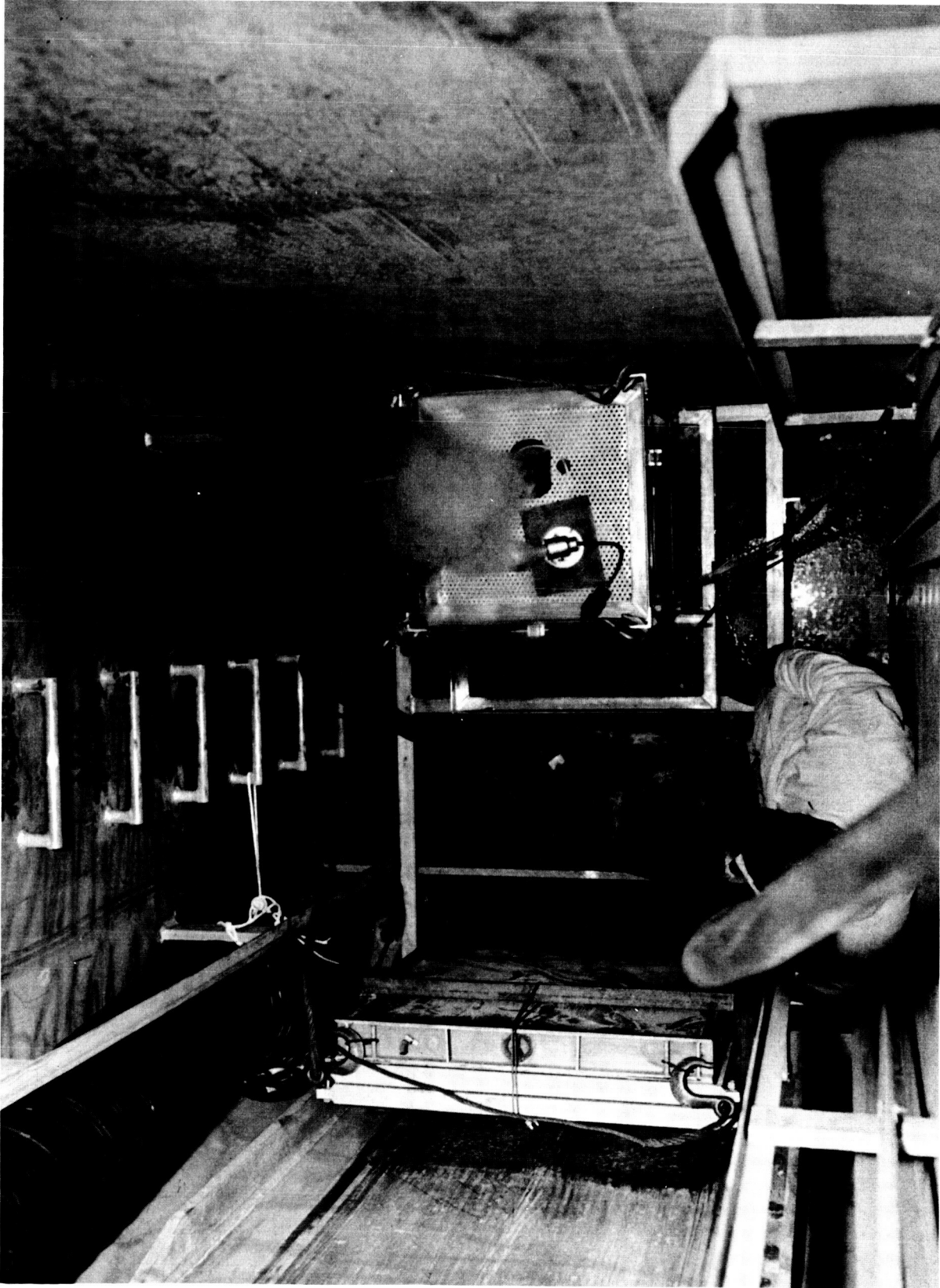


Figure 6 Dewar-Pallet Assembly in the OAT

LN₂ supply valve which, in turn, was connected to a similar line that led to the test dewar. Pneumatic operation of this valve was accomplished by manual control of a Bristol recorder-controller mounted in the radiation-effects console in the control room of the NARF facility (Fig. 7).

The cryogen liquid level was monitored by the four resistors and six of the thermocouples (Fig. 8). The resistors were connected to an instrument designed to indicate immersion of the resistors. Cryogen coming into contact with the resistors resulted in a large increase in resistance, which triggered a light on the facility instrument panel corresponding to a particular liquid level. The upper six probe thermocouples (T1 through T6) were fed into a series of Bristol recorders with a range of +100 to -450°F, and the temperature monitored by a dial and also continuously recorded on chart paper. The lowest thermocouple on the probe, TB, was used to monitor specific temperature changes of the mixture of LN₂ and LOX occurring during the experiment, near the bottom of the dewar. This thermocouple was connected to a Rubicon potentiometer for accurate temperature determinations.

4.2.2 Test Procedure

The special pallet assembly in which the open-mouth dewar was installed was placed at the irradiation site in the OAT test tank by crane, where it remained throughout the entire experiment (Fig. 9). The appropriate connections were made

*Not available on Experiment No. 1

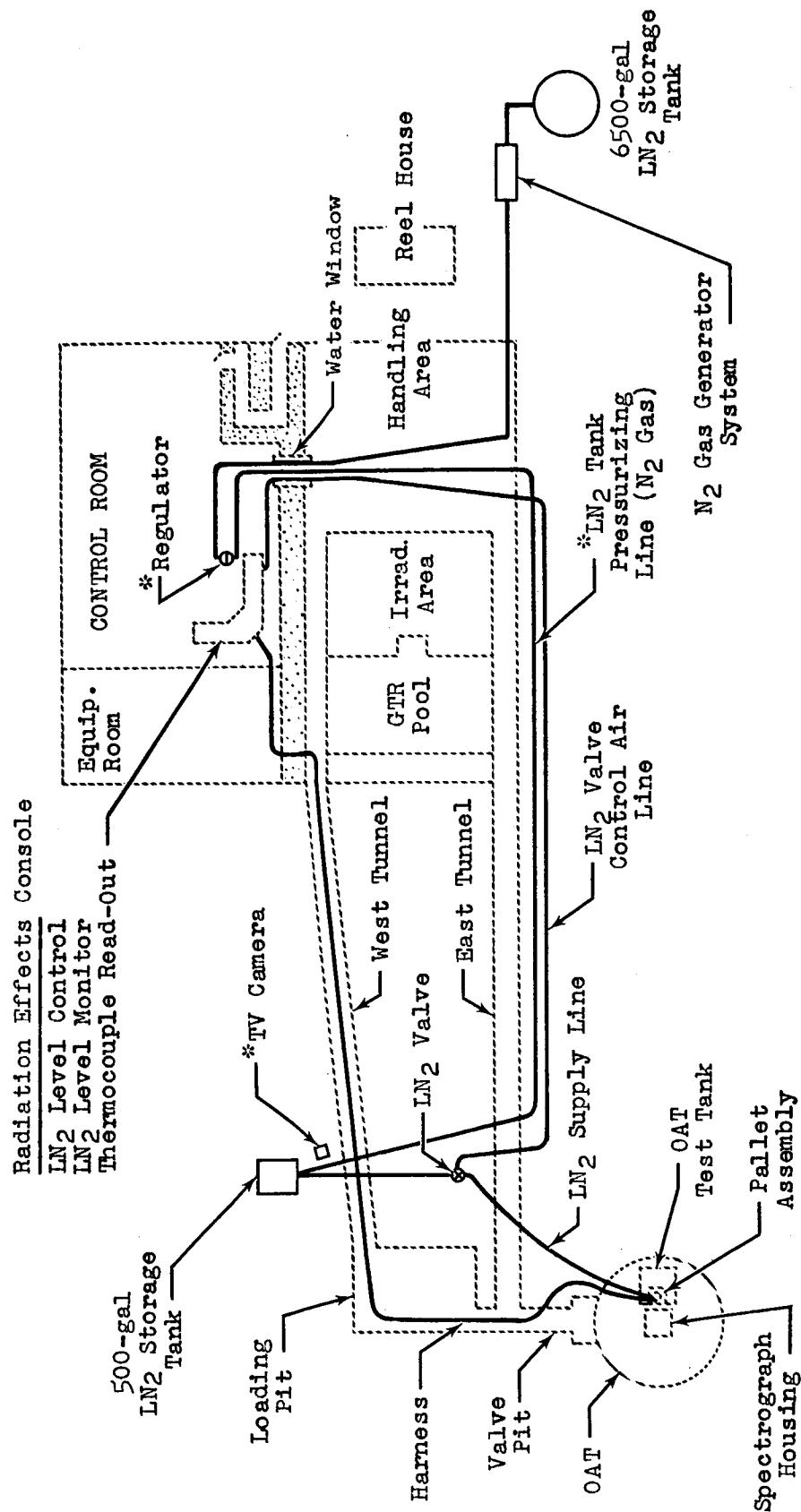


Figure 7 Accessory Equipment: Open-Dewar Experiments

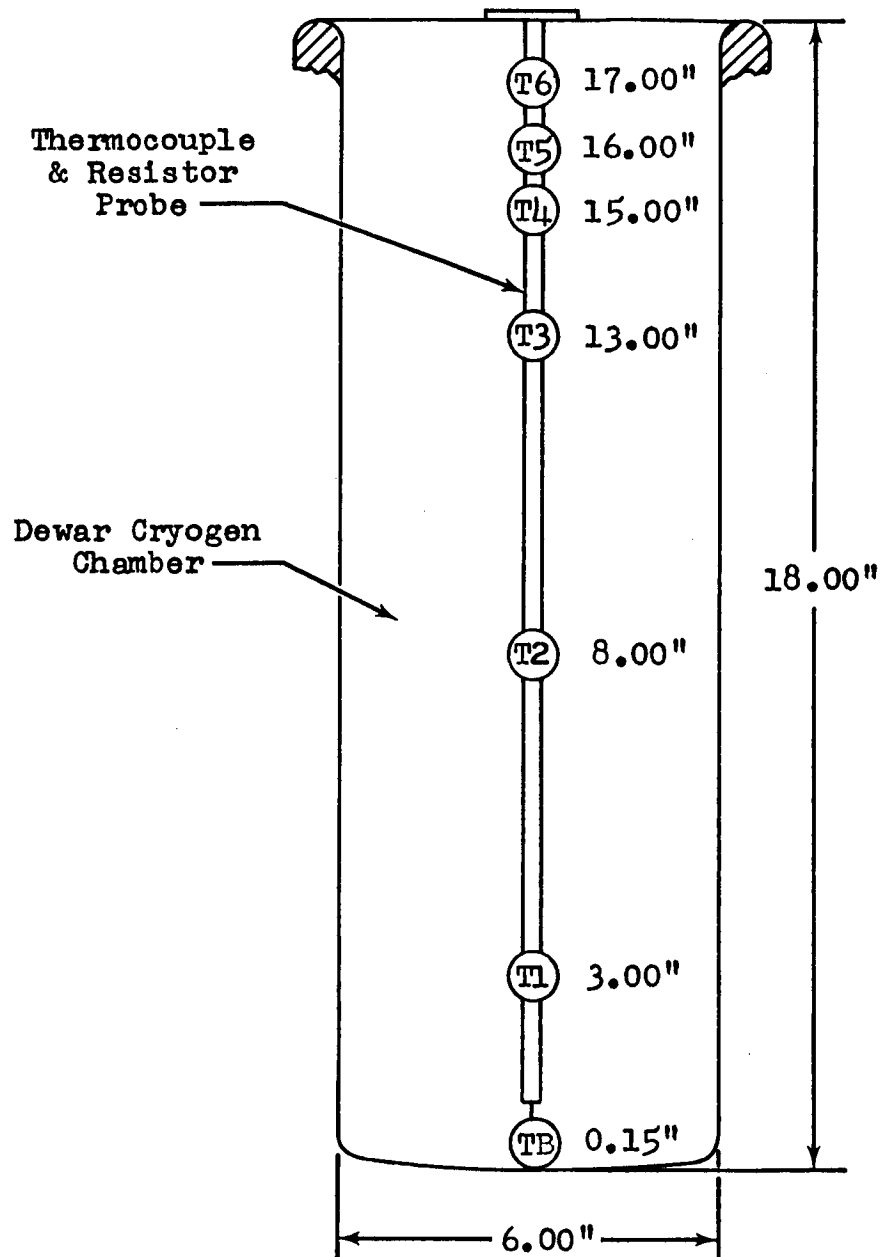
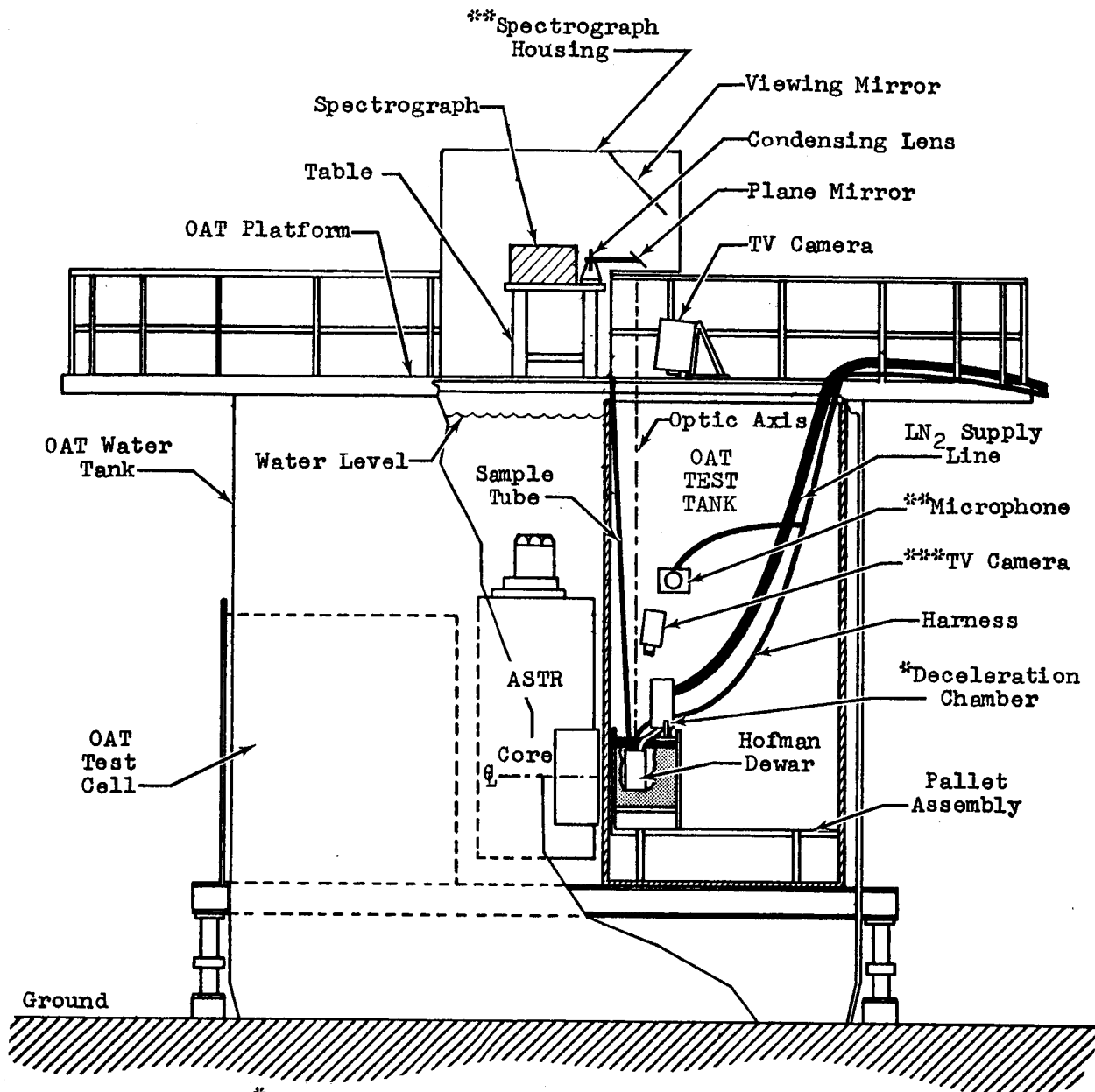


Figure 8 Liquid-Level Probe Positions for Open Dewar



*Not available on Experiment No. 1
 **Not available on Experiment No. 1 and No. 2
 ***Not available on Experiment No. 1 and No. 3

Figure 9 Experimental Arrangement: Open-Dewar Experiments

to the liquid-nitrogen supply line and the liquid-level probe harnesses. Approximately 1 hr before the start of the irradiation, two liters of LN_2 were poured manually into the test dewar with a small dewar. Then 0.75 liter of liquid oxygen was added to the test dewar by the same method. The test dewar was then filled to within 4 in. of the top with the LN_2 supplied remotely from the 500-gal tank.

The open-mouth dewar and its contents were then irradiated for 40 Mw-hr, during which time the liquid level was supposedly maintained at a position approximately 4 in. from the top of the dewar. Upon completion of the irradiation, the LN_2 supply was turned off and the contents of the dewar allowed to begin boiling off.

The spectrograph and accessories (Figs. 10 and 11) were placed in position on top of the OAT test tank so that the dewar could be viewed while the boil-off continued. Later, the boil-off rate was increased by passing ambient nitrogen gas into the dewar.

4.2.3 Test Results and Conclusions

There were no incidents of explosions during this experiment. Observations of the different instrumentation indicated what was believed to be the eventual loss of the liquid-oxygen portion of the mixture in the dewar a few minutes after irradiation of the dewar began. The temperature of the thermocouple close to the bottom of the dewar approached and leveled off

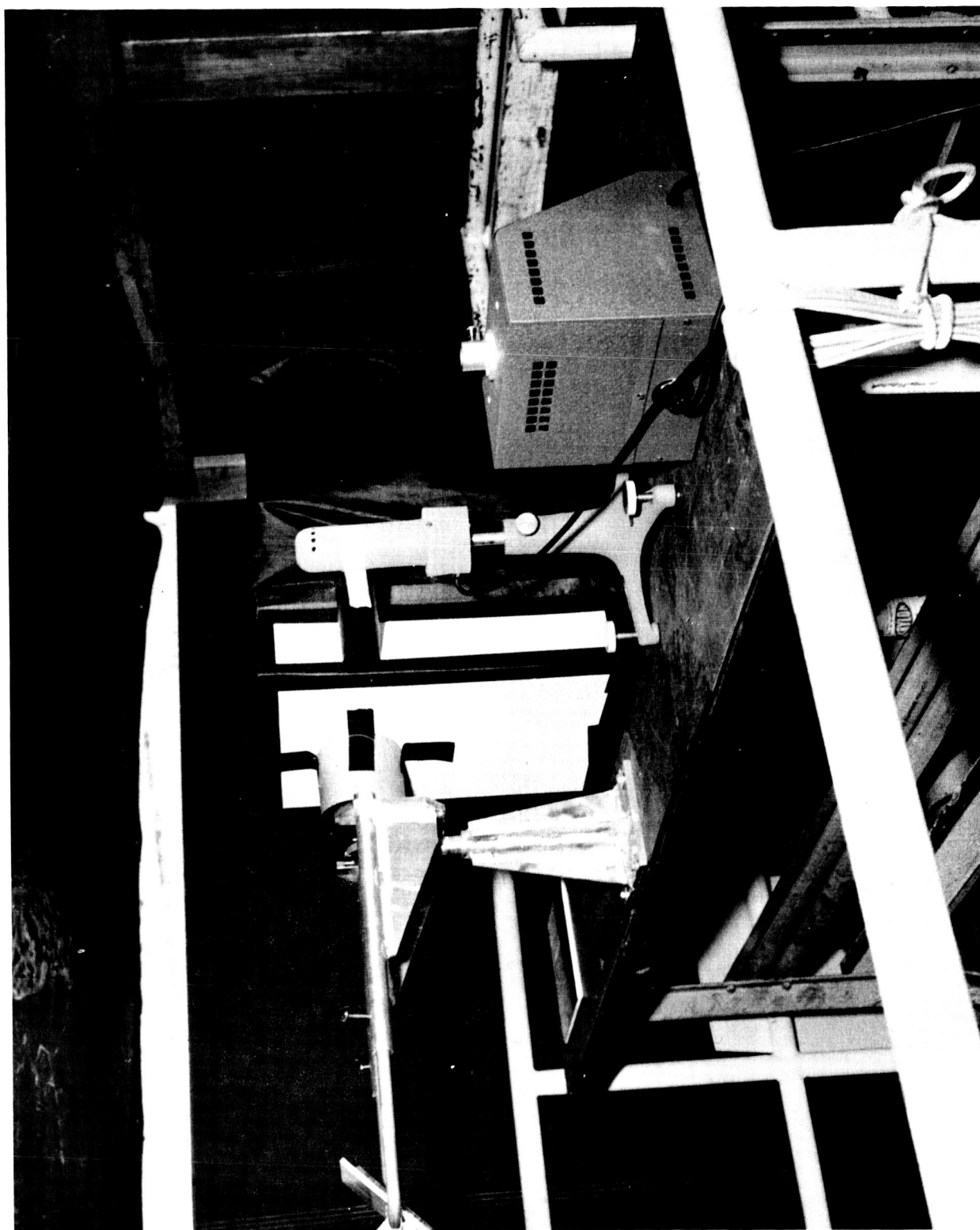


Figure 10 Spectrograph Setup

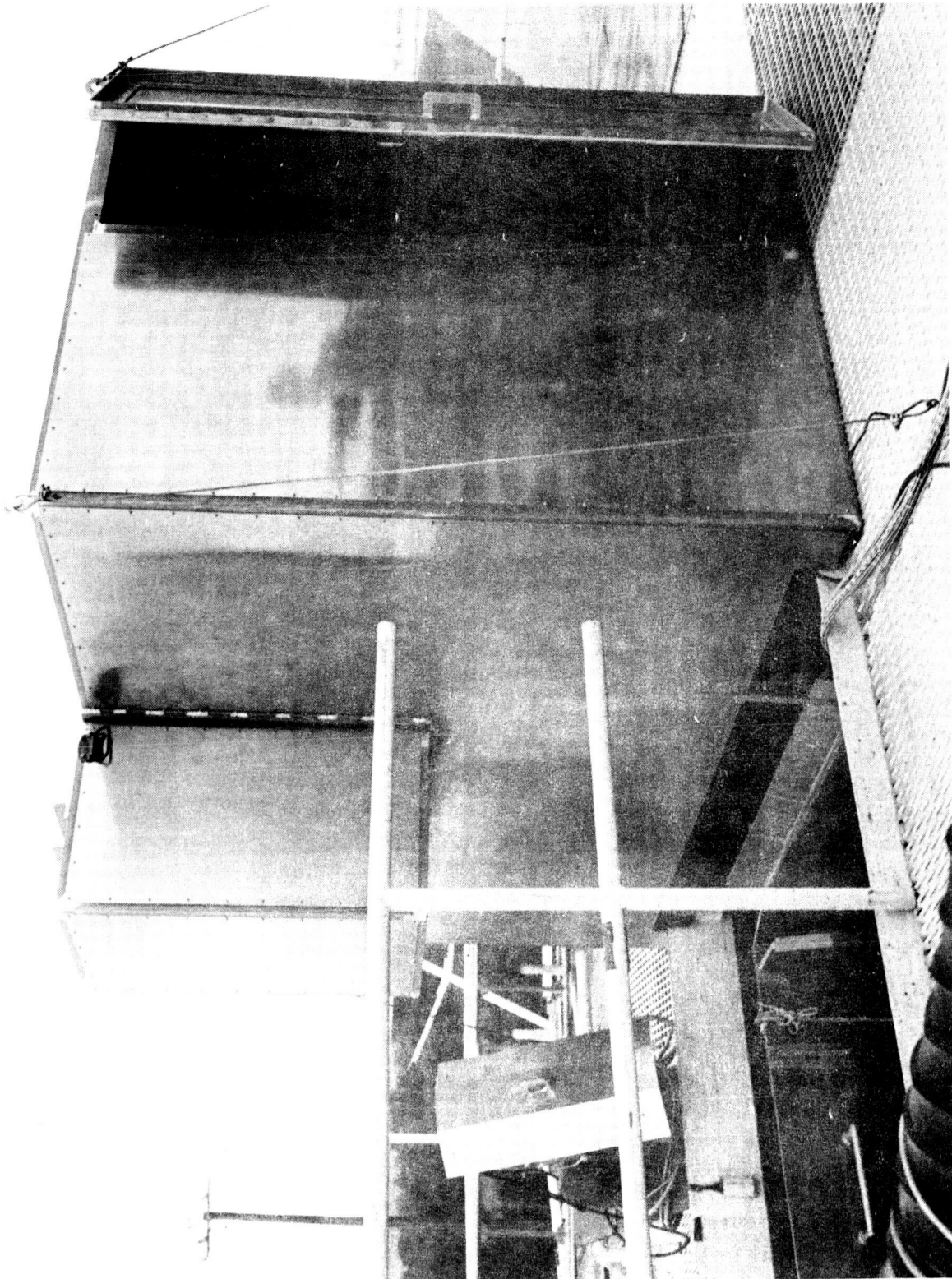


Figure 11 Spectrograph Housing on OAT Catwalk

at LN_2 temperature after being somewhat erratic at first.

Difficulties were experienced in maintaining proper liquid-level control, especially under the remote operating conditions in a nuclear reactor field. The problems were believed to be due to a combination of conditions - remote location of the LN_2 source tank; tank pressure; the necessary location of the test dewar inside the OAT test tank, requiring the LN_2 supply line to run from ground level up to a height of 20 ft and thence drop 13 ft down to the test dewar - all of which resulted in providing an undesirable amount of 2-phase flow. The large amount of gas present under interrupted LN_2 flow arising from line warmup caused splashing of the LN_2 in the test dewar during attempts to maintain the liquid level. This resulted in excessive use of LN_2 during the experiment, as indicated by low tank-gage pressure at the end of this run.

It was concluded that the next experiment would be conducted with a deceleration chamber (dewar) and an open dewar incorporating baffles to ensure that the above-mentioned 2-phase flow would be reduced to a minimum.

4.3 Experiment 2: Open-Dewar Test (30 April 1964)

4.3.1 Test-Equipment Description

The equipment incorporated in Experiment 2 was nearly the same as that for Experiment 1. The main changes were the addition of an aluminum deceleration chamber for better

LN₂ flow control, three aluminum baffle plates in the test dewar; and three television cameras in and around the OAT test tank.

A device was needed to minimize the 2-phase flow entering the test dewar during the first test. As described earlier, 2-phase flow occurs as a result of interrupted liquid flow and change in flow rates in the supply lines. This problem necessitated the design and construction of a vacuum-walled "deceleration" chamber (Fig. 12). By this arrangement, the supply line enters a port in the chamber near the top and is tangential to the inner wall. This allows the 2-phase fluid to "spin" around the inner wall and to separate the liquid centrifugally from the gas phase. A small port provided at the bottom of the chamber allows the liquid to drain off by gravity; a small baffle in the bottom portion of the chamber reduces liquid "swirling" action at this drain port. A much larger port at the top of the chamber releases the generated gas to the air.

The deceleration chamber was mounted on top of the dewar-pallet assembly, as shown in Figure 13. An insulated copper drain tube was installed from the bottom port of the deceleration chamber, over the edge of the cutout, and down to a point 2 in. below the inside lip of the test dewar.

To provide a smooth liquid surface in the test dewar (especially in the area where the liquid-level sensing points

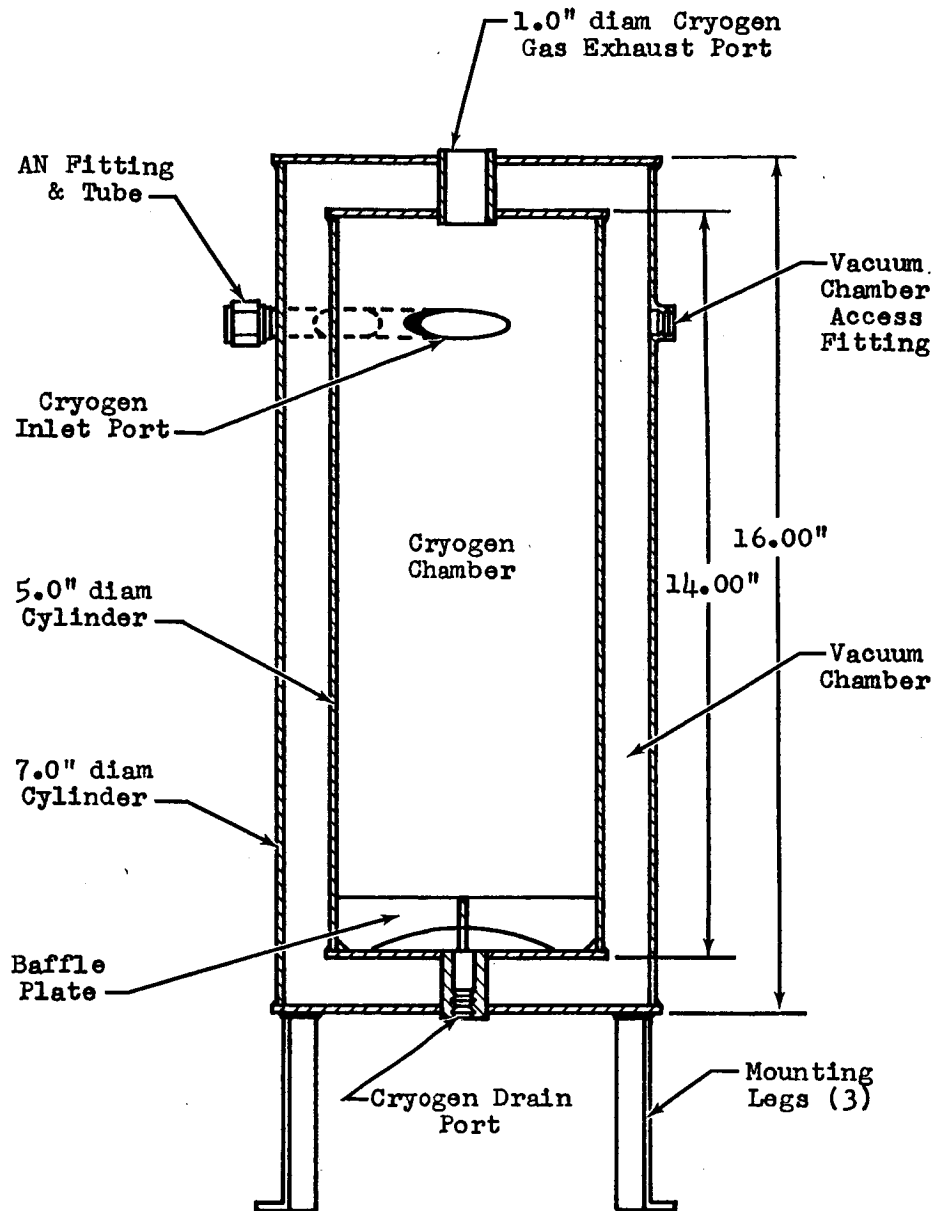


Figure 12 Deceleration Chamber

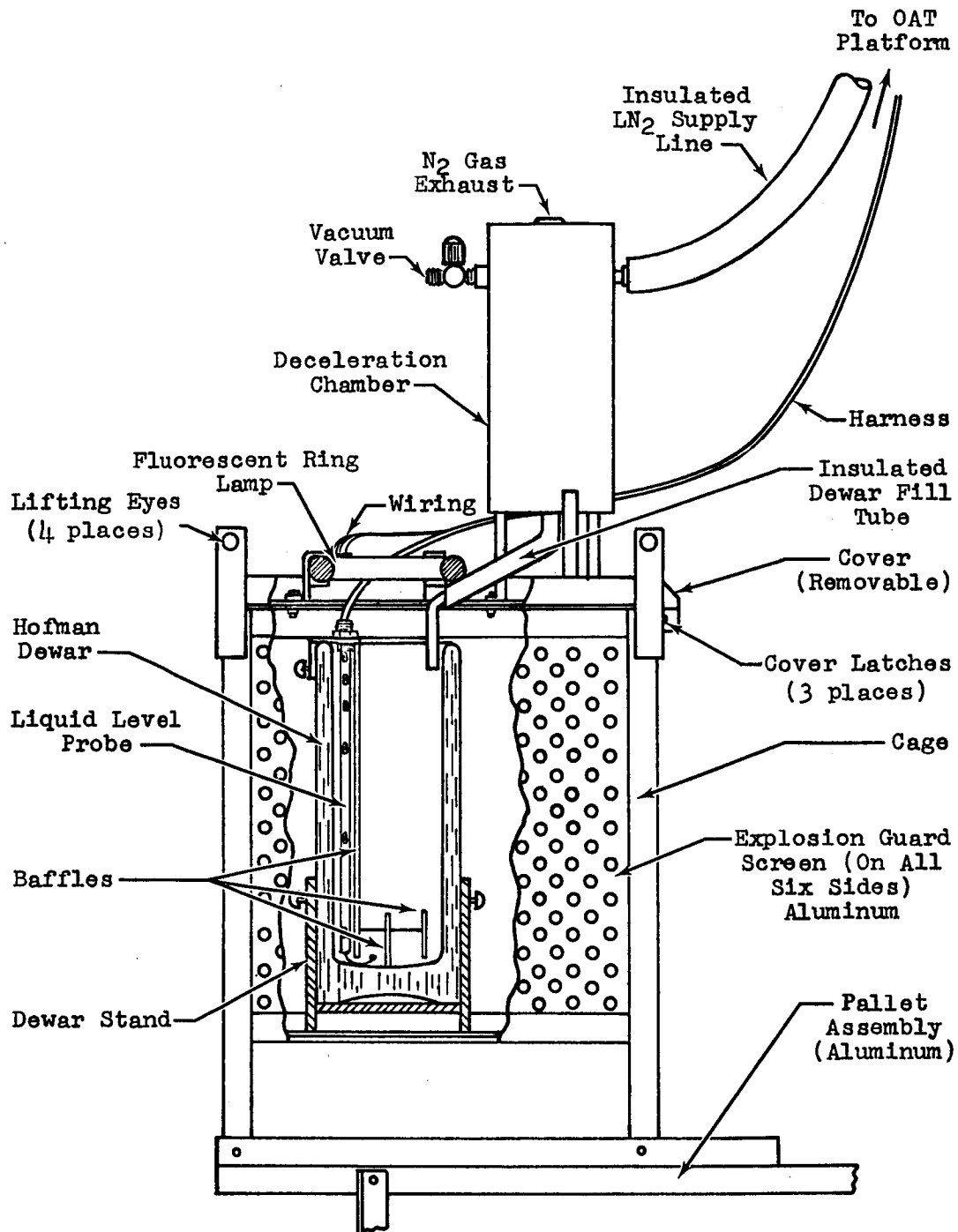


Figure 13 Test Assembly: Open-Dewar Experiments 2 and 3

were located), a baffle plate was welded to the mounting bracket and extended from the top to nearly the bottom of the dewar. This baffle protected the liquid-level probe from the more vigorous liquid action expected in the remaining area of the dewar. Two small baffles were also placed near the bottom of the dewar.

Three television cameras were used. One was set up near the 500-gal LN_2 supply tank to view the pressure gage on the tank from the control room. A second camera was temporarily mounted on a wall inside in the OAT test tank near the pallet assembly to view the test dewar and deceleration chamber from the control room. A third camera was placed on the top platform of the OAT to be moved into position, after the irradiation portion of the experiment, to view the test dewar during the boil-off period of the liquid in the dewar. The positions of the three television cameras are shown in Figure 9.

The movable incandescent lamp used in the previous experiment to aid in aligning the optics was replaced by a 25-w fluorescent ring lamp of 6 in. inside diameter. This ring lamp and its retaining bracket were mounted and centered above the hole cut out in the top plate of the dewar-pallet assembly cage (Fig. 13). This arrangement allowed the ring lamp to remain in place during the entire experiment, since it did not obstruct the view of the interior of the test dewar and could readily be used for checkout of the optical alignment

when needed.

4.3.2 Test Procedure

The dewar-pallet assembly containing the open-mouth dewar and deceleration chamber was placed in position at the irradiation site in the OAT test tank. The instrumentation hardinesses and cryogen supply line connections were made and the end of the sample drop tube anchored in place over the opening of the dewar.

An hour before the start of the irradiation period, two liters of LN_2 was added to the test dewar, using the LN_2 supplied remotely from the 500-gal tank. Then 1.50 liters of liquid oxygen was added by the method used in Experiment 1. The test dewar was then filled to within 4 in. of the top with additional LN_2 remotely supplied.

The reactor was then brought up into position and to power at 8 Mw for a period of about 20 min. During this time, observations using the installed TV camera were made of the test dewar and deceleration-chamber environmental operating characteristics under irradiation conditions. After it was decided that the system operation was satisfactory, the reactor was lowered to enable the removal of the TV camera from the OAT test tank. This procedure was necessary because of the high radiation dose that would have resulted in the eventual operational loss of the unit.

The reactor was again raised and brought back to power

for the continuation of the irradiation run. During this time, the liquid level in the dewar was maintained at between 13 and 15 in. from the bottom of the dewar.

During the early periods of irradiation, the 500-gal LN_2 supply tank pressure was varied by a regulator adjustment of the N_2 gas pressurizing line in the control room to ascertain the optimum tank pressure for various LN_2 flow conditions. The TV camera viewing the tank gage showed this pressure to be about 27 psi.

The first third of the 40-Mw-hr run was conducted at a power level of 8 Mw; the latter two thirds, at 10 Mw.

The thermocouples on the liquid-level probe were observed visually throughout the irradiation while the liquid level using the resistor sensors was maintained. Except for the period noted in Section 4.3.3, operation of the entire system proved to be much more satisfactory than that used in Experiment 1.

Near the completion of the irradiation run, the LN_2 supply was shut off and the contents of the dewar allowed to begin boiling off. When the radiation background level had dropped somewhat, the spectrograph, spectrograph housing, and accessories were placed in position on top of the OAT to begin monitoring the test dewar. Also, the TV camera on the platform of the OAT was moved into position at the edge of the test tank to view down, at an angle, at the dewar.

4.3.3 Test Results and Conclusions

Approximately one hour before shutdown time, thermocouples T3, T4, and T5 (Fig. 8) suddenly ceased functioning and remained inoperative for the rest of the experiment. The incident was thought to be the result of an explosion that occurred in the vicinity of the surface of the liquid, which at the time was just above R1 and at the probe. This was borne out later, when an examination of the region revealed considerable fraying of the Fiberglas insulation - more so than at other points close to this area.

This explosion, however, did not seem to change the level of the liquid to any degree. A few minutes before shutdown, a decision was made to shut off the liquid flow to allow reactor heat to lower the level of the liquid (the boil-off rate was calculated earlier to be approximately 2 gal/hr at 10 Mw) to about 8 in. above the bottom of the dewar by the time the irradiation run was complete. This prediction was reasonably accurate since T2 (located 8 in. above the bottom of the dewar) came out of liquid 6 min after shutdown.

Another explosion, apparently self-initiated, occurred about $1\frac{1}{4}$ hr later. The spectrograph was in place on the OAT catwalk, but the background level of radioactivity was too high (~ 400 mr/hr) to expose photographic film. At the time of the explosion, the liquid level in the dewar was below T2 but above T1, probably about 5 in. above the bottom of

the dewar. The explosion was not observed on the TV camera and recorders in the control room because personnel had been removed earlier as a safety precaution, when Health Physics monitors reported the possibility of air contamination.

Moments after the explosion, the dewar was viewed from the top of the OAT tank with the aid of a flashlight and the viewing mirror in the spectrograph housing (Fig. 14). Missing was the large aluminum baffle plate - which was found the next morning approximately 15 ft north of the OAT. The fluorescent ring lamp and its mounting bracket were not in position on top of the cage. Pieces of darkened glass were scattered about the OAT and the OAT platform; a few pieces were found in the spectrograph housing. The ring lamp mount was later found wrapped around the southwest (lead-water tank) guide rail of the OAT test tank, held there by the electrical wiring (Fig. 15). The liquid-level probe and its mounting bracket were wedged halfway under the top plate (guard screen) of the cage; the other end of the probe was still affixed to the electrical cables.

It appeared at the time of viewing the dewar through the mirror as if the bottom of the dewar were missing. To check this, a cotter pin was inserted into the sample tube while the dewar was being observed through the large mirror in the spectrograph housing. After the pin passed through the tube, another (second) explosion occurred. This induced

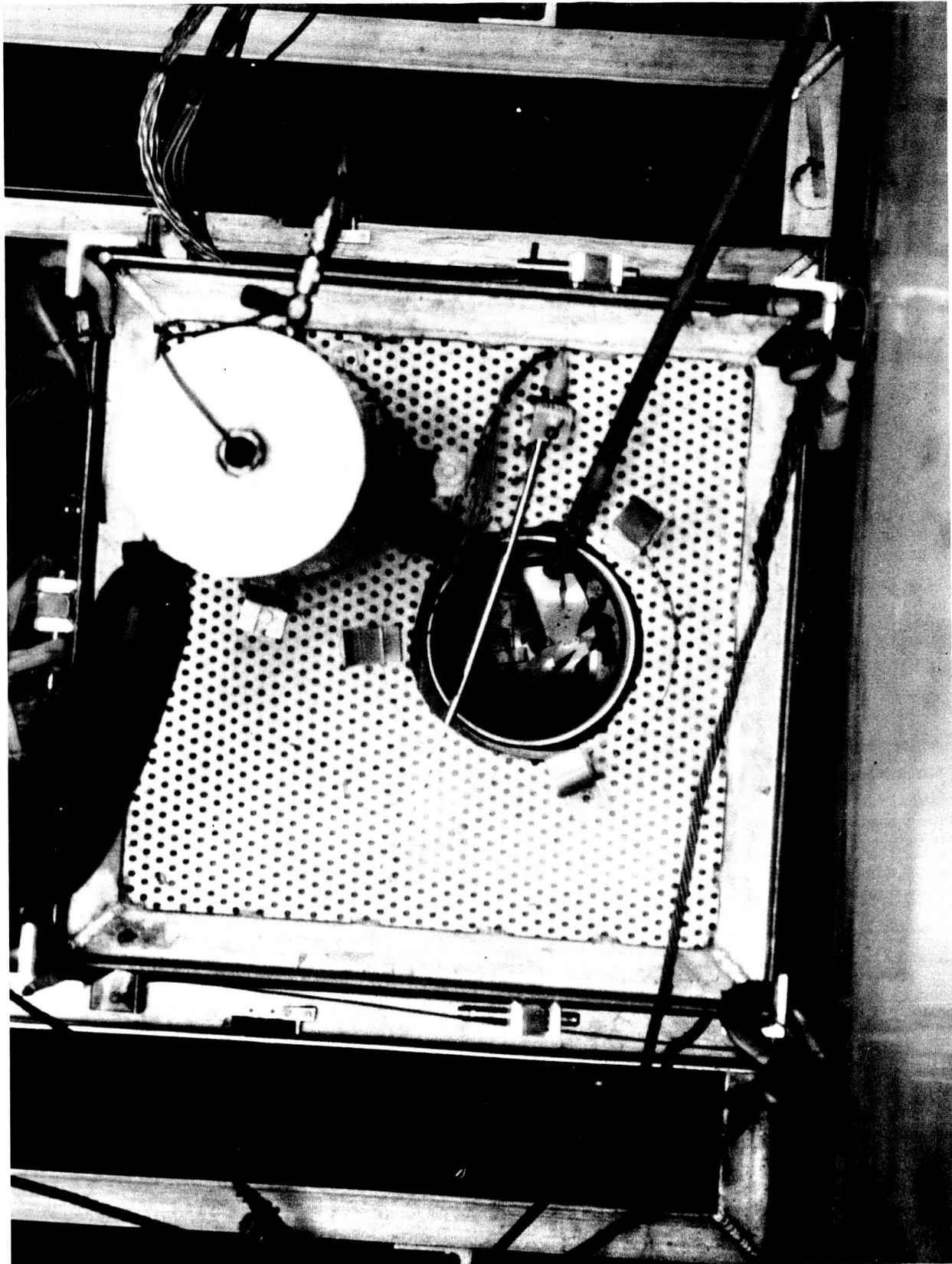


Figure 14 Close-Up of Top of Test Assembly: Experiment 2

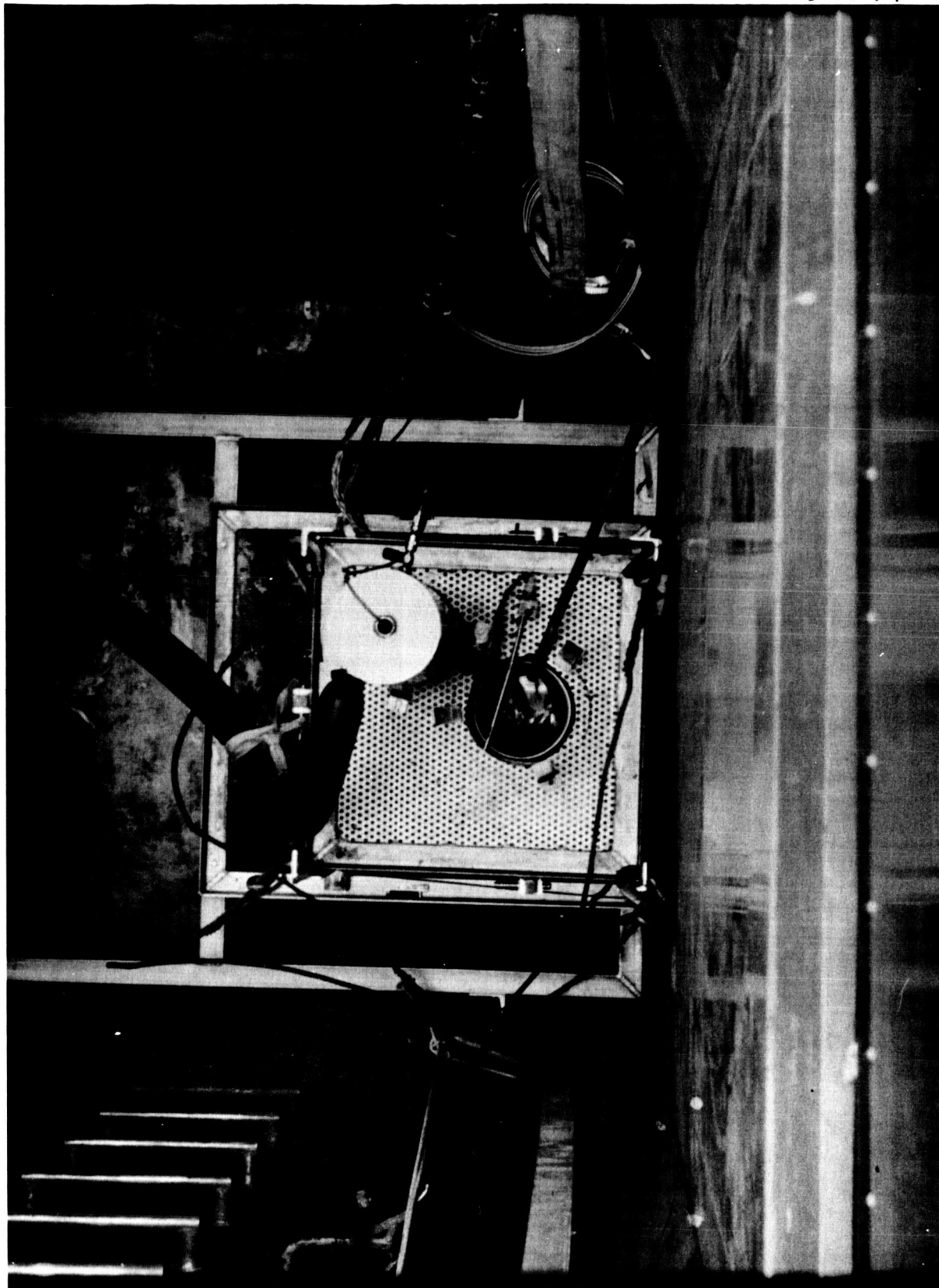


Figure 15 Long Shot of Test Assembly: Experiment 2

explosion was somewhat weaker in sound intensity than the first (self-initiated) explosion, although still fairly intense. Visual observation of this explosion indicated a flash of light whose luminosity was probably intense enough to be recordable with the spectrograph. No further explosions occurred after this point in the experiment.

Examination of the test dewar a few days after the two explosions showed that the inner wall had not ruptured, although the lower one-quarter section of the inner wall was dented considerably. Close examination of the aluminum baffle plate showed it to be badly buckled on the lower end (Fig. 16). The area and nature of the buckling of this plate, the plate's originally installed position in the dewar and location with respect to the liquid-level probe, and the location of the dent in the inner wall of the dewar lead to the conclusion that the first postirradiation explosion must have originated at a point nearly 4 in. from the bottom of the dewar (at about the liquid level at that time), near or at the liquid-level probe. This explosion forced the baffle plate over against the opposite side (inside) of the dewar and then up and out of the dewar. It was noticed that the bottom $1\frac{1}{2}$ in. of the aluminum baffle plate was corroded as if it had been chemically acted upon prior to initiation of the explosion that blew it out of the dewar (Fig. 16).

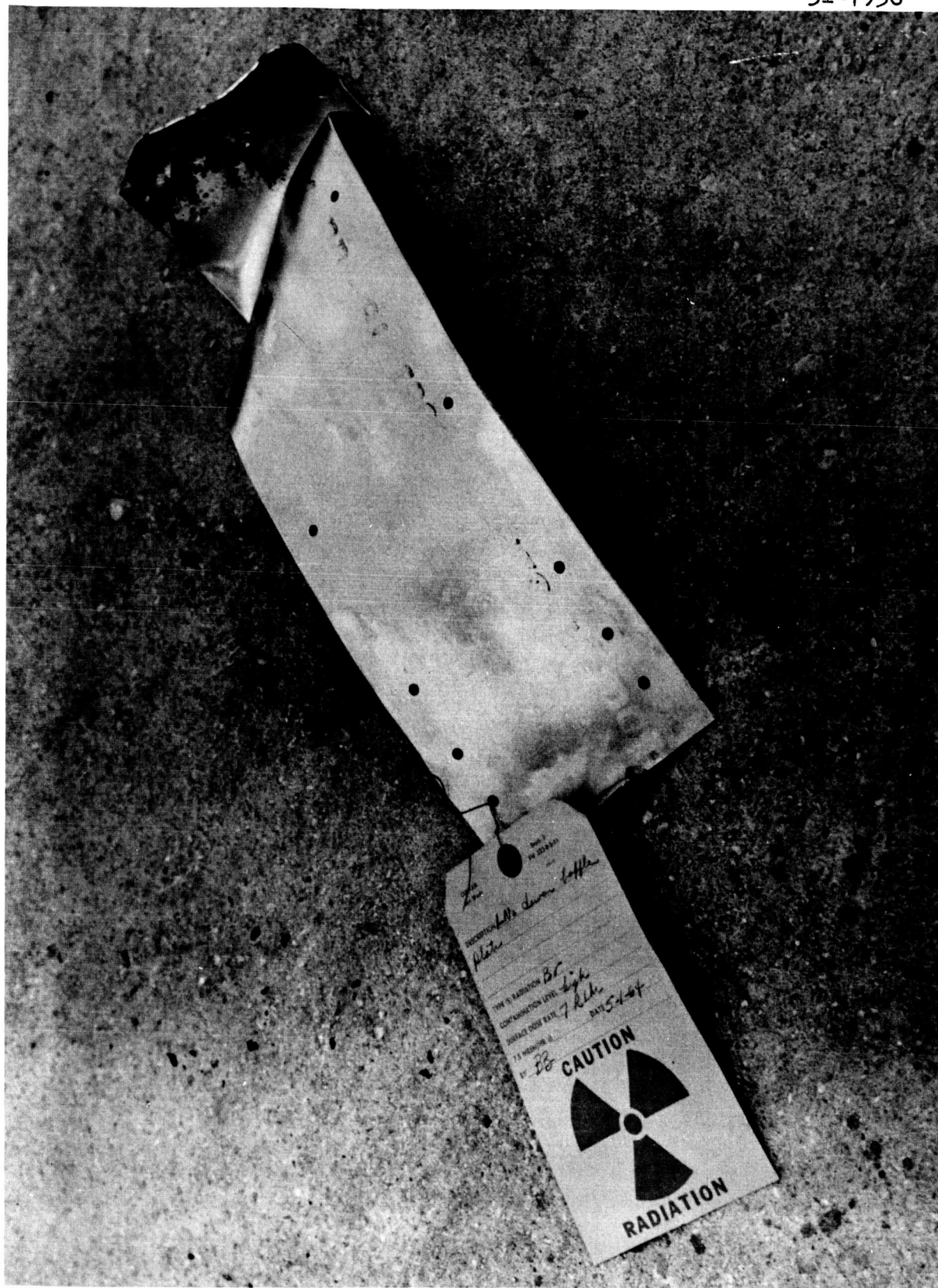


Figure 16 Baffle Plate after Experiment 2

4.4 Experiment 3: Open Dewar Test (12 and 13 May 1964)

4.4.1 Test-Equipment Description

Only a few changes were made in the equipment used in this test from that used in Experiment 2 (30 April 1964)

The further use of an aluminum baffle plate in the test dewar was considered undesirable. It not only represented an explosion hazard (blown out of the dewar in the earlier test), but also provided an additional volume that increased boil-off of liquid due to gamma heating as well as an additional surface area on which products of irradiation might collect to produce an explosive condition. Hence, the baffle was removed.

A new dewar and liquid-level probe were fabricated for this experiment. The design of the liquid-level probe was altered slightly, especially in the lower half of the probe. This was done to ensure the absence of any construction material which could possibly react in some way with the products formed by irradiation, especially within a liquid level up to 10 in. from the bottom of the dewar. "Ceramo" thermocouple wire replaced the Fiberglas-insulated wire used previously for the construction of T1 and T2 thermocouples in the probe. The thermocouple located on the bottom of the dewar, TB, was eliminated for this test, and T1 was moved down 2 in. to a new location (Fig. 17). The Ceramo consisted of copper-constantan 22-gage wire, with ceramic insulation and a stainless-steel

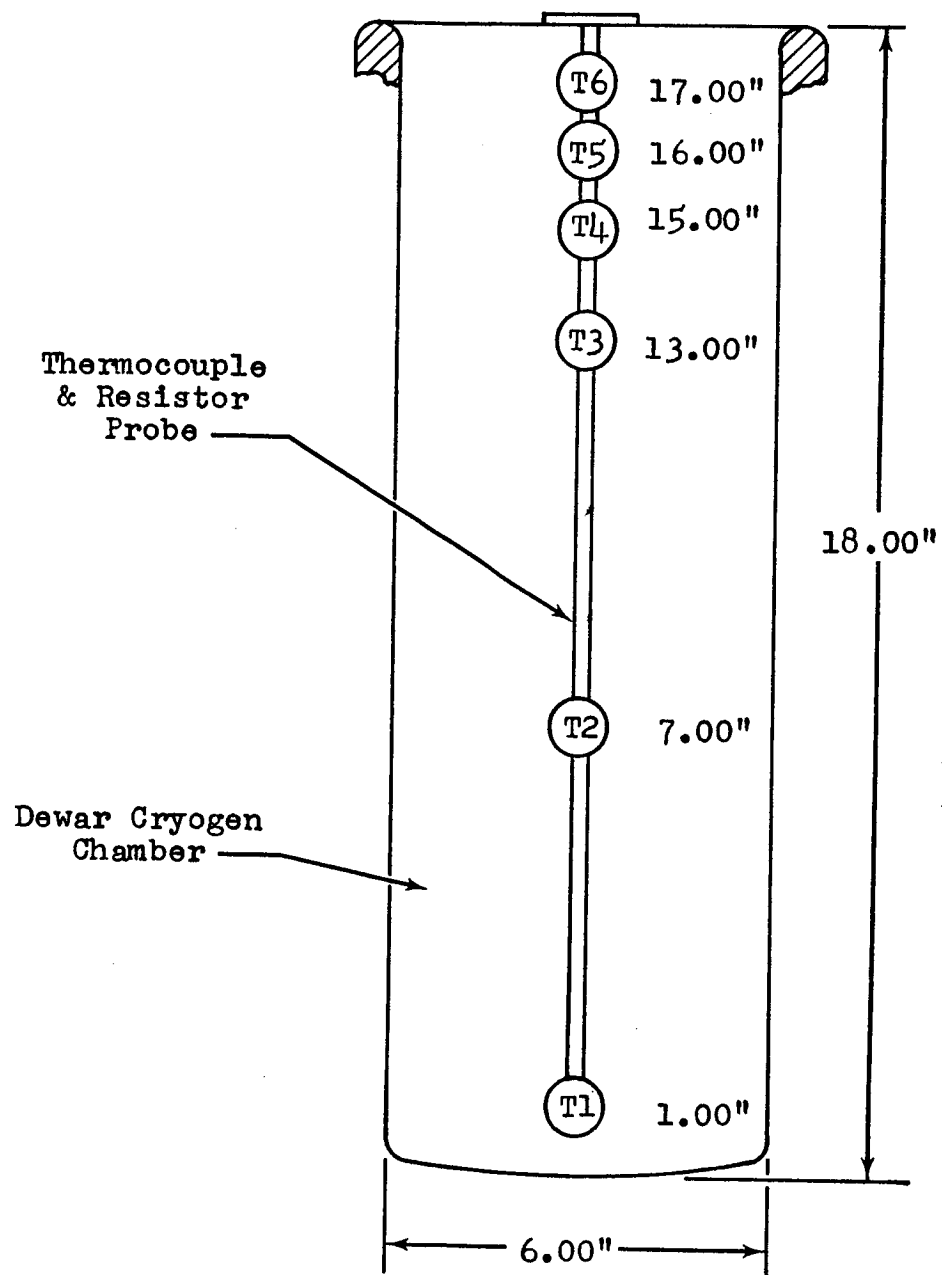


Figure 17 Modified Liquid-Level Probe Positions for Open Dewar

sheath of 1/8-in. diameter. The Ceramo wire used for T1 and T2 was connected to Fiberglas-insulated lead wire leading from the probe. All the thermocouples and lead wires in the probe would have been replaced by the Ceramo wire for this experiment had there been more in stock. This wire minimized the possibility of crevices (which more than likely existed in the fibrous insulation) that could trap irradiation products and thus possibly give rise to explosions at several places above the bottom of the dewar. The resistors were mounted in the same manner as in the previous two experiments.

A heavy tarpaulin was available for this experiment to be tied down over the top of the OAT test tank after the irradiation run to prevent flying debris from leaving the test tank during explosions. A 1-ft-diam hole was cut in the tarp above the opening of the test dewar to provide a viewing area for the spectrograph. Due to the obstruction of viewing area presented by the tarp, the use of a television camera located in the past experiments on the OAT platform was discontinued. Relocation of the camera down into the test tank below the tarp was considered, but a camera attachment point from which the inside of the dewar could be seen was not easily available.

A microphone suspended down inside the OAT test tank near the test dewar (Fig. 9) enabled personnel in the control room to have an audible indication of the events occurring in the dewar and in the surrounding area during the experiment.

4.4.2 Test Procedure

The pallet assembly containing the open-mouth dewar and deceleration chamber was set in place at the irradiation site in the OAT test tank by crane. The instrumentation harness and the LN_2 supply line were connected as in Experiment 2. The end of the sample drop tube was positioned over the edge of the dewar opening (Fig. 9).

Approximately an hour before the beginning of the irradiation period, $2\frac{1}{2}$ liters of LN_2 was added to the test dewar. The $1\frac{1}{2}$ liters of liquid oxygen was added with a hand dewar. The test dewar was then filled up to a level 14 in. from the bottom with additional LN_2 remotely supplied, and the level was maintained between 13 and 15 in. throughout the irradiation run. The reactor was raised and the power brought up to 10 Mw, where it remained for the duration of a 40-Mw-hr run.

The techniques used on earlier tests of monitoring the dewar thermocouples, resistors, corresponding temperatures, and liquid level were repeated during this test. The use of a microphone near the dewar proved a very valuable aid toward the better understanding of the sequence of events occurring in the OAT test tank during the course of the experiment. For the most part, the systems operated satisfactorily, except as indicated in Section 4.4.3.

At the completion of the irradiation run, liquid flow to the dewar was shut off with the level at nearly 15 in.

from the bottom of the dewar, and the boil-off procedure was initiated. Within $1\frac{1}{2}$ hr, the spectrograph equipment was placed in position and the first exposure was made. The background level at this time was less than 200 mr/hr.

4.4.3 Test Results and Conclusions

A series of 20 explosions of varied intensities were picked up by the microphone suspended in the OAT test tank during the entire open-dewar experiment. Fifteen of these occurred during the 4-hr, 10-Mw irradiation run, which ended at 2103 hours on May 12. Three of the six original thermocouples and three of the four resistors became inoperative as a result of these explosions. Only T1, T2, T6, and R1 (Fig. 17) remained to be monitored during the postirradiation period. The Rubicon potentiometer of this experiment was reading the temperature of T1, since TB had been deleted in this probe. The remaining thermocouples were being monitored by the Bristol recorders.

Following is a log of the sequence of events recorded over a period which covered the irradiation run and the boil-off period of the dewar:

May 12

1703: at power at 10 Mw
1815: audible small intensity
pop (explosion)
1825: small pop

May 13

0145: smelled ozone while
on OAT platform
0246: Rubicon reading of T1
erratic (occurring about
every 20 sec)

May 12

1828: small pop
1851: small pop
1903: small pop
1905: small pop
1906: loud pop
1909: medium pop
1913: small pop
1914: medium pop (lost T5)
1919: small pop
1949: medium to loud pop
(lost T4 and R3)
2016: small pop
2020: small pop
2025: small pop (lost T5
and T3)
2103: shutdown of reactor
2155: first exposure with
spectrograph equipment

May 13

1301: Rubicon galvo driven off
scale; turbulence also
noticed on Bristol Re-
corder of T2 (still in
liquid)
1305: cannot balance Rubicon
because of too much
turbulence
0305: continued agitation of
0315: T2 and T1
0345: radiation background
150 mr/hr at spectro-
graph
0432: initiated pop in dewar
with a metal-rubber
specimen
0715: T2 out of liquid
1008: small pop
1009: small pop
1719: Rubicon shows T1 coming
out of liquid reading
82° K approx.
1723: T1 reading 102°K
1729: 108°K
1734: 113°K
1739: 122°K
1743: 130°K
1745: intense explosion; T1
reading approx 132°K
before becoming inoperative
as a result of the explo-
sion. T2 also lost at
this time.

From the above sequence of events it is possible to draw several conclusions. The explosions during the irradiation run were all at or above the level of the liquid in the dewar at the time. Destruction of some of the lower thermocouples was due to severing of the corresponding leads higher on the probe. Some of the products formed by the irradiation were probably trapped around the wires, insulation, and resistors in the upper half of the probe (the section of the probe was not altered in design from that of the earlier experiments), and were initiated in much the same way as occurred in the preceding test. The part of the probe (lower half) in which Ceramo wire was used provided a "cleaner" area from conditions necessary for producing an explosion, but not an "exclusion" area from explosions as borne out by the sequence of events.

The relatively small explosion that was induced at 0432 hours on May 13 by a metal-rubber specimen was not intense enough to be registered on the spectrogram, which showed, upon development, only some background fogging of the film. The most intense explosion (spontaneous) occurred in the final moments of the experiment at 1745 on May 13, when all the LN_2 had boiled off. However, the background (daylight) was too high to expose the fast Polaroid film in the spectrograph.

The excessive amount of time that was required (far beyond that expected) to boil off the liquid contents of the dewar has not been fully explained. However, the presence of approximately

one liter of water, found in the dewar after the experiment, may shed some light on the matter. This water might have been in a frozen state and thus acted as insulation over the surface of the liquid nitrogen to slow down the rate of boil-off after reactor shutdown. Furthermore, although heavy metal specimens placed into the specimen drop tube were heard to rattle down in the tube, they were not heard to hit the bottom of the dewar, as in the second experiment - again, an indication that a formation of ice might be present.

Further examination of the dewar after the experiment revealed little or no damage to the walls. The contents of the dewar included the afore-mentioned metal specimens that had been dropped therein to initiate explosions and a brownish-red suspension in the water. An analysis of the clear liquid (brownish-red suspension removed) by a Nestler's colorimetric test indicated a concentration of 10 mg/liter of ammonium ion. Analysis of the brownish-red suspension showed a presence of iron oxide. This was probably formed (1) in the oxidation of the steel samples used in attempts to initiate explosions and (2) in oxidation occurring thereon up to the time that the dewar contents were examined a few days later, when the radioactivity background had subsided somewhat.

It is believed that the final explosion occurred when thermocouple T1, located at a point about 1 in. above the bottom of the dewar, was above the liquid surface and was not

measuring the change of temperature within the remaining liquid after all the LN_2 had boiled out of it. It is not known why the Rubicon reading of T1 and the temperature of T2 were erratic during the half-hour period from 0245 to 0315 on May 13. Perhaps a chemical reaction of some type was in progress. The simplicity of the instrumentation almost rules out any trouble of this nature, and checks were made on this at the time.

The length of time required in complete boil-off within the dewar led to the various difficulties of recording spectrographically explosions as related above. In the hour preceding the time of the final explosion, arrangements were being made to begin taking exposures again at dusk, but the final explosion occurred about an hour before darkness set in. In later closed-dewar experiments, the system was designed incorporating a "light pipe" opened only to the dewar and spectrograph so that absolute darkness would be unnecessary during exposure of photographic film.

4.5 Experiment 4: Closed-Dewar Test (9 September 1964)

4.5.1 Test-Equipment Description

Experiment 4 was the first of two closed-dewar tests. The closed dewar used in each case was designed and manufactured at NARF specifically for these experiments. The closed dewar (Figs. 18, 19, 20) consists of the following component parts: a vacuum-walled cryogen chamber, a cover plate, a window mounting

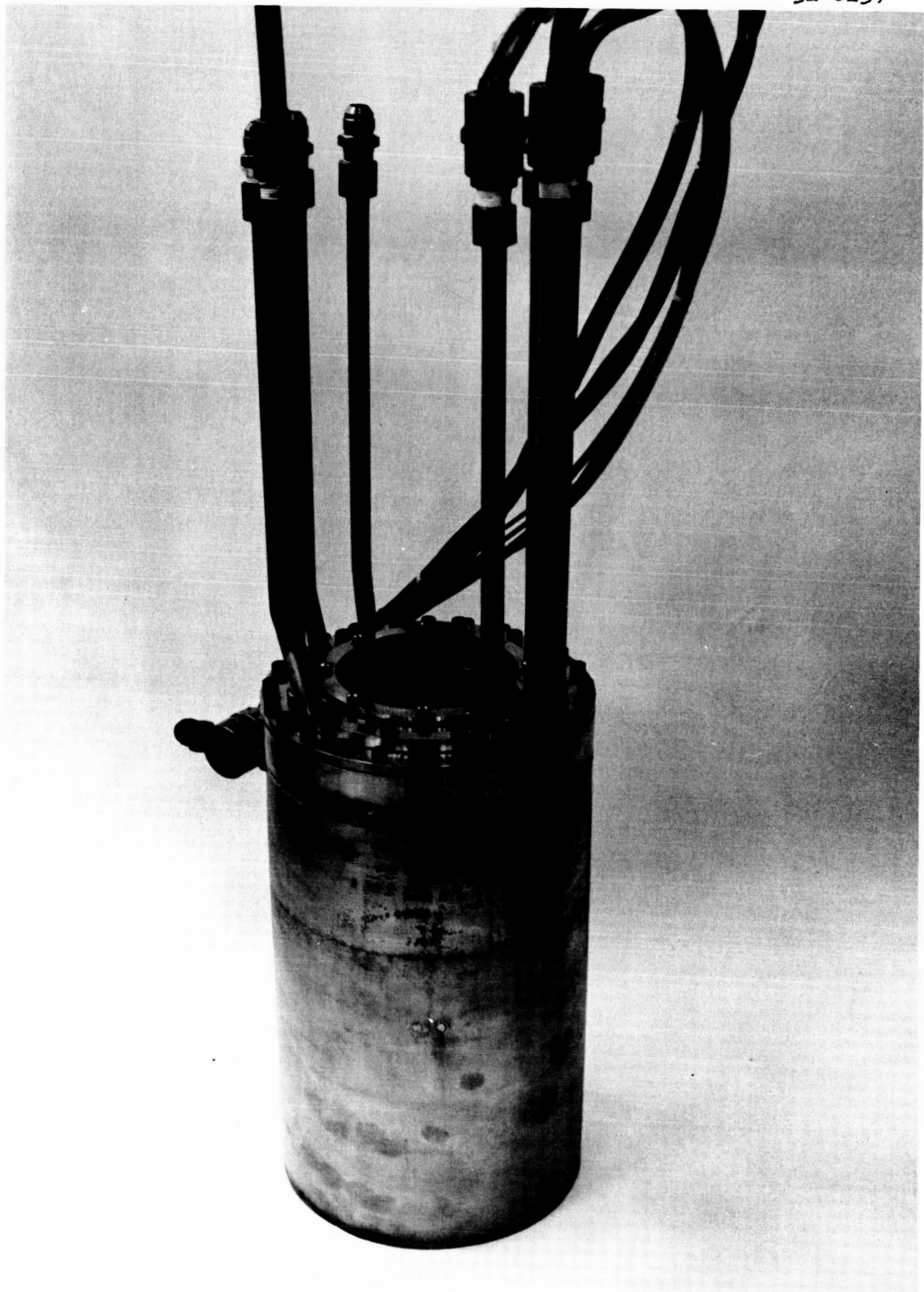


Figure 18 Closed Dewar with Fittings and Window

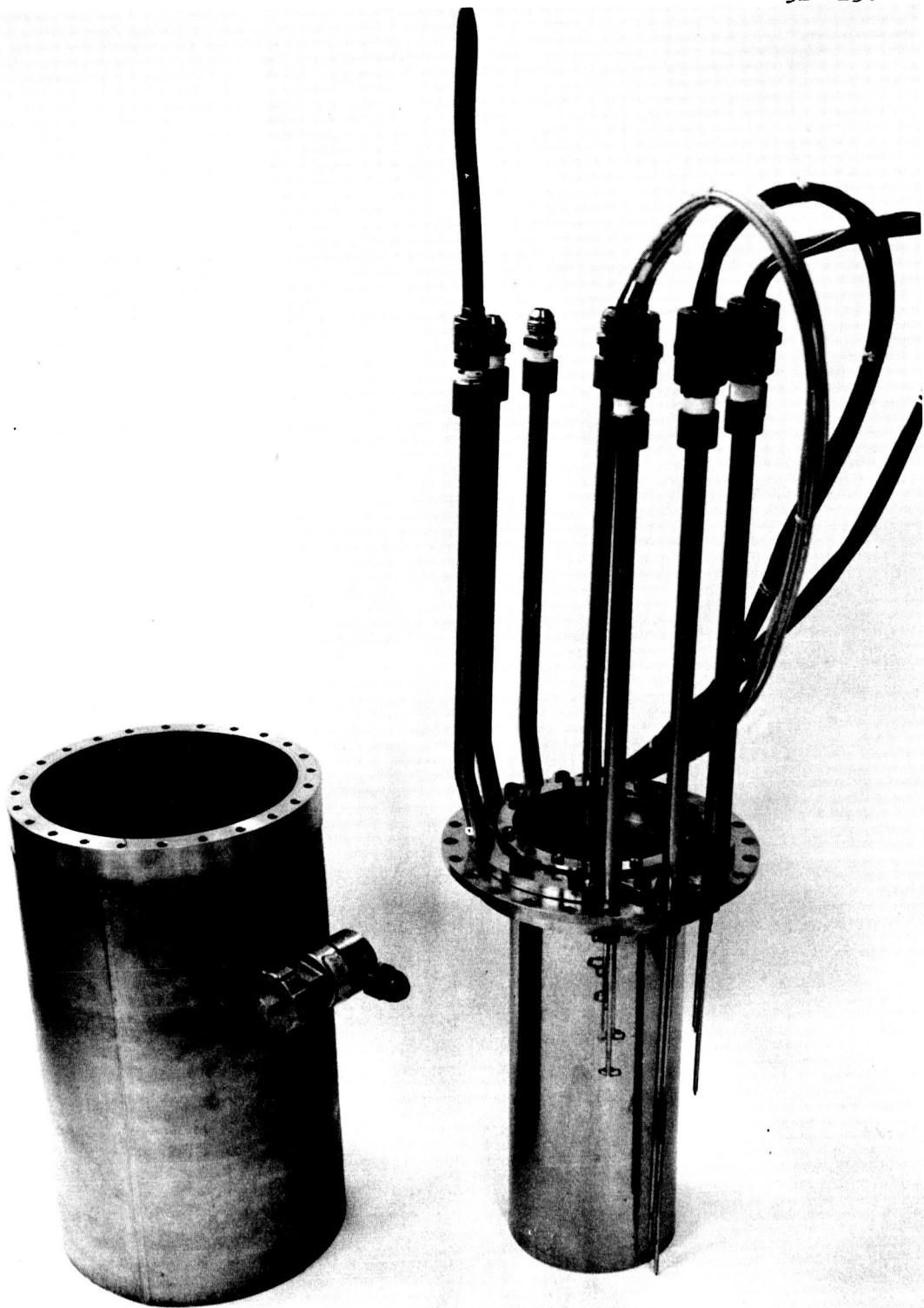


Figure 19 Disassembled Closed Dewar

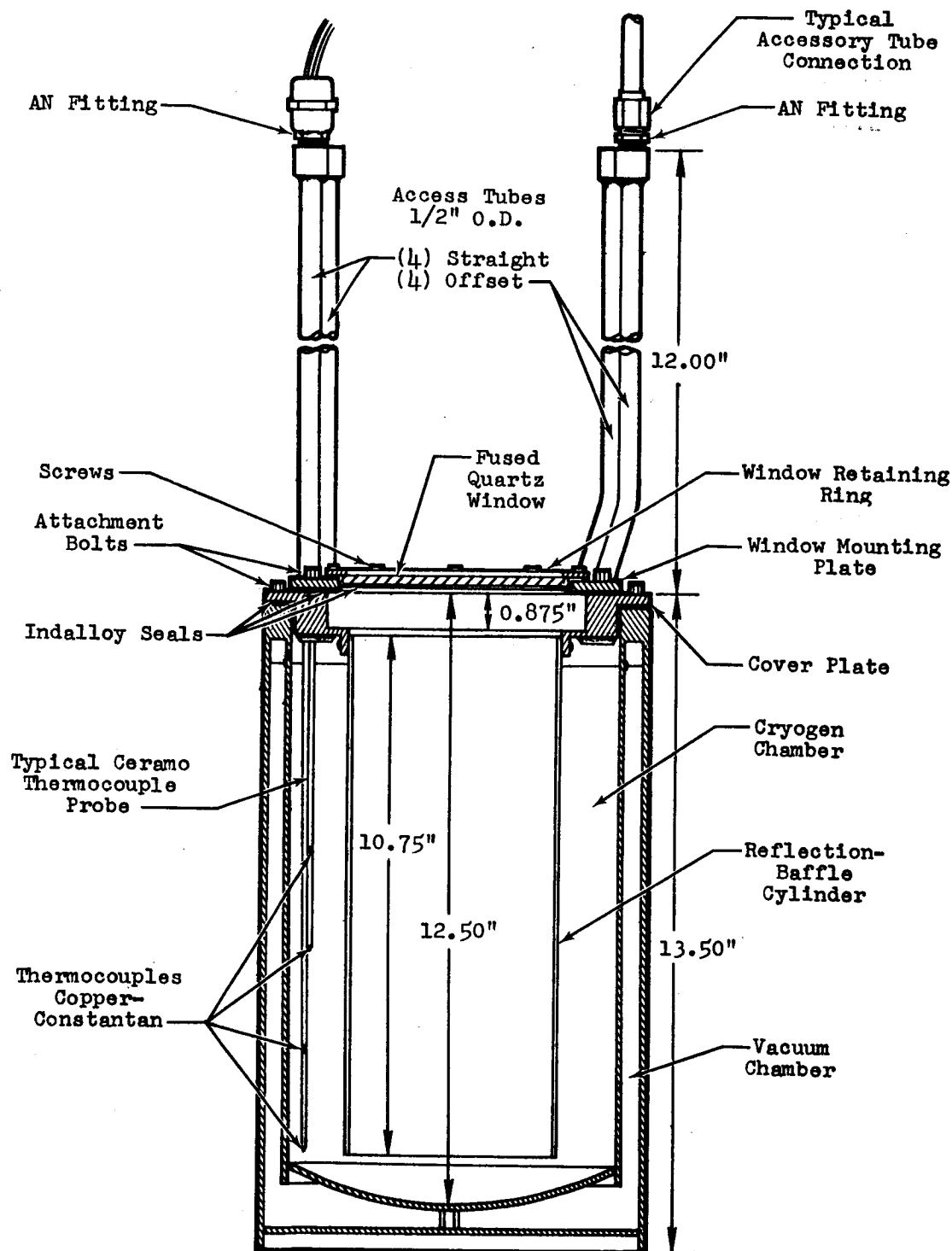


Figure 20 Schematic of Closed Dewar

plate, a window, and a window retaining ring. The metal parts were constructed of stainless steel.

The cover plate was designed to provide permanent provisions for eight stainless-steel tubes, which were welded to the plate. These allowed access to the inside of the cryogen chamber with the following: a cryogen inlet, a cryogen gas exhaust, a sample inlet, thermocouple sensor probes, resistor liquid-level probes, an overpressure relief valve, and pressure and acoustic monitoring probes. Also, the cover plate provided an opening of 4.51-in. diameter to allow optical access through a window to the bottom of the dewar during the experiments. The 4.5-in.-diam x 0.25-in.-thick window was to be made of a "radiation-resistant" GE type 151 fused silica. However, because fabrication problems prevented the manufacturer (General Electric) from providing these in time for the experiments, a substitute window of GE type 101 fused quartz was installed for these experiments.

Attachment of the cover plate to the dewar and the window mounting plate to the cover plate were effected with Allen-head bolts. The window retaining ring secured the window to the window mounting plate by means of screws. A pressure seal was effected between the plates and between the plate and the window with a 0.060-in.-diam gasket of Indalloy solder. A thick-walled stainless-steel cylinder 4.5 in. in diameter x 10.8 in. long was attached to the bottom of the cover plate

to be used as a baffle and a light reflector for explosions. The inside surface of the bottom plate of the cryogen chamber was polished to give a high-reflecting surface to aid in the spectrographic recording of the luminous events. The vacuum chamber of the dewar was pumped down to five microns before the experiment.

Two thermocouple probes using Ceramo wire were constructed (Fig. 19). Each probe consisted of four copper-constantan 22-gage wire ceramic-insulated, 1/8-in.-OD stainless-steel-sheathed Ceramo wires mounted in a threaded fitting for attachment in the access tubes. The area between the wires was blocked with Indalloy solder to provide a pressure-tight seal in the probe. The resistor liquid-level probe was also constructed of Ceramo wire. This probe consisted of four copper-copper 22-gage wire, ceramic-insulated, 1/8-in.-OD stainless-steel-sheathed Ceramo wires mounted in a threaded fitting for attaching to the access tube. The area between the wires was also blocked with Indalloy solder. A 100-ohm 1/4-w carbon resistor was soldered in place on the end of each wire (Fig. 19).

To provide safe confinement of the closed dewar during and after the irradiation and alignment of the dewar with the spectrograph and associated equipment, the special aluminum frame (dewar-pallet assembly) constructed for the open-dewar tests was modified for use with the closed dewar (Fig. 5). The 8-in.-diam hole in the top screen of the explosion-guard

cage was enlarged to a 14-in. diameter to allow clearance through the hole for the eight cryogen-chamber access tubes with the dewar installed in the pallet assembly. These access tubes extend up to a point about 2 in. above the screen to facilitate the installation and removal of accessory equipment and cryogenic lines from the dewar.

A relief valve, set to relieve at 10 psi, was installed on a dewar access tube as a safety precaution against over-pressurizing the cryogen chamber during the tests (Fig. 21). The chamber, however, had been previously tested successfully to a pressure of 30 psi with the fused-quartz window installed.

An acoustic monitor box containing a 3-in.-diam paper-cone microphone was installed for listening in on the cryogen chamber in the dewar for any audible events that might occur during the experiment. A 1/2-in. copper tube was used to connect from a dewar access tube to the monitor box located some 14 ft away. The box was located outside the irradiation site to minimize radiation damage thereto (Fig. 21). A pressure transducer, an IRC potentiometer type having a range of from 0 to 30 psi and mounted on the monitor box, measured the internal (cryogen chamber) pressure of the dewar.

A 1/2-in. copper sample tube was attached to one of the access tubes. Through this tube, specimens were dropped during the postirradiation period of the experiment in the course of studying catalytic effects. Another access tube was connected

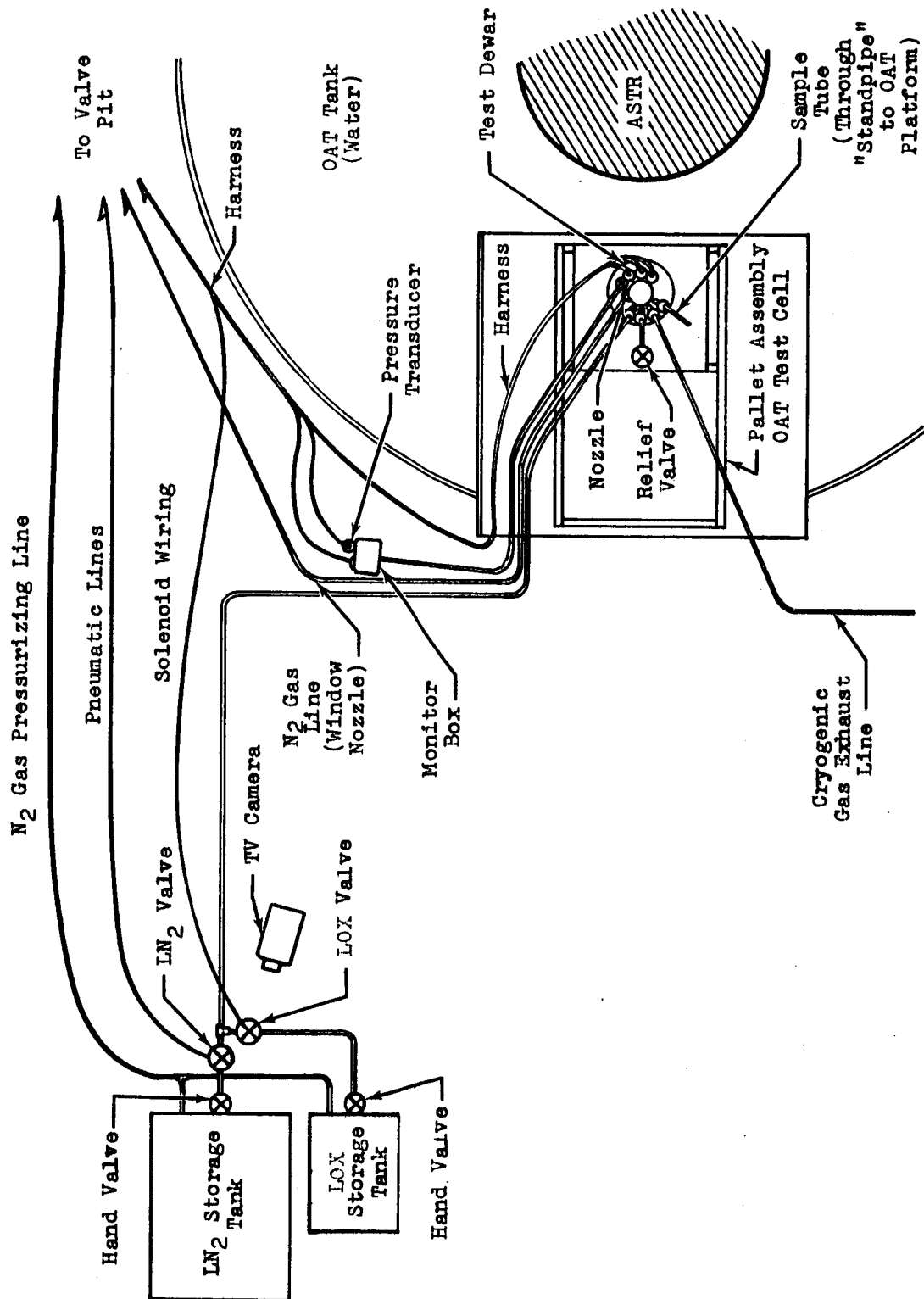


Figure 21 Accessory Equipment in OAT Area: Closed-Dewar Experiments

to a 1/2-in. insulated copper tube that served as the exhaust line for the cryogenic gases from the dewar cryogen chamber. This line was vented to the atmosphere in an area outside the irradiation site (Fig. 21).

The test cell of the OAT was chosen as the irradiation site in the closed-dewar experiments instead of the OAT test tank used in the open-dewar experiments. The test cell is accessible from the side of the OAT and is close to ground level, thus enabling the cryogen supply tanks and accessory equipment to be placed much closer to the test dewar with cryogen supply lines (Fig. 22) of minimum length.

A 500-gal liquid-nitrogen tank containing a pure grade of LN_2 (<200 ppm O_2) was placed near the OAT tank (Fig. 21) and connected to a pneumatically operated variable control LN_2 supply valve by an Armaflex-insulated 1/2-in. copper line. A 50-gal liquid-oxygen (LOX) tank was located near the LN_2 tank and connected to an insulated 1/2-in. copper line that ran to a solenoid-operated (normally closed) valve. The output of the pneumatic and solenoid valves was "manifolded" together and a 3/8-in. insulated copper line run from this point to the irradiation site and connected to an access tube on the dewar.

The LN_2 and LOX tanks were pressurized remotely through a line from the control room by adjusting a regulator that was tied into a nitrogen-gas generation system supplied with

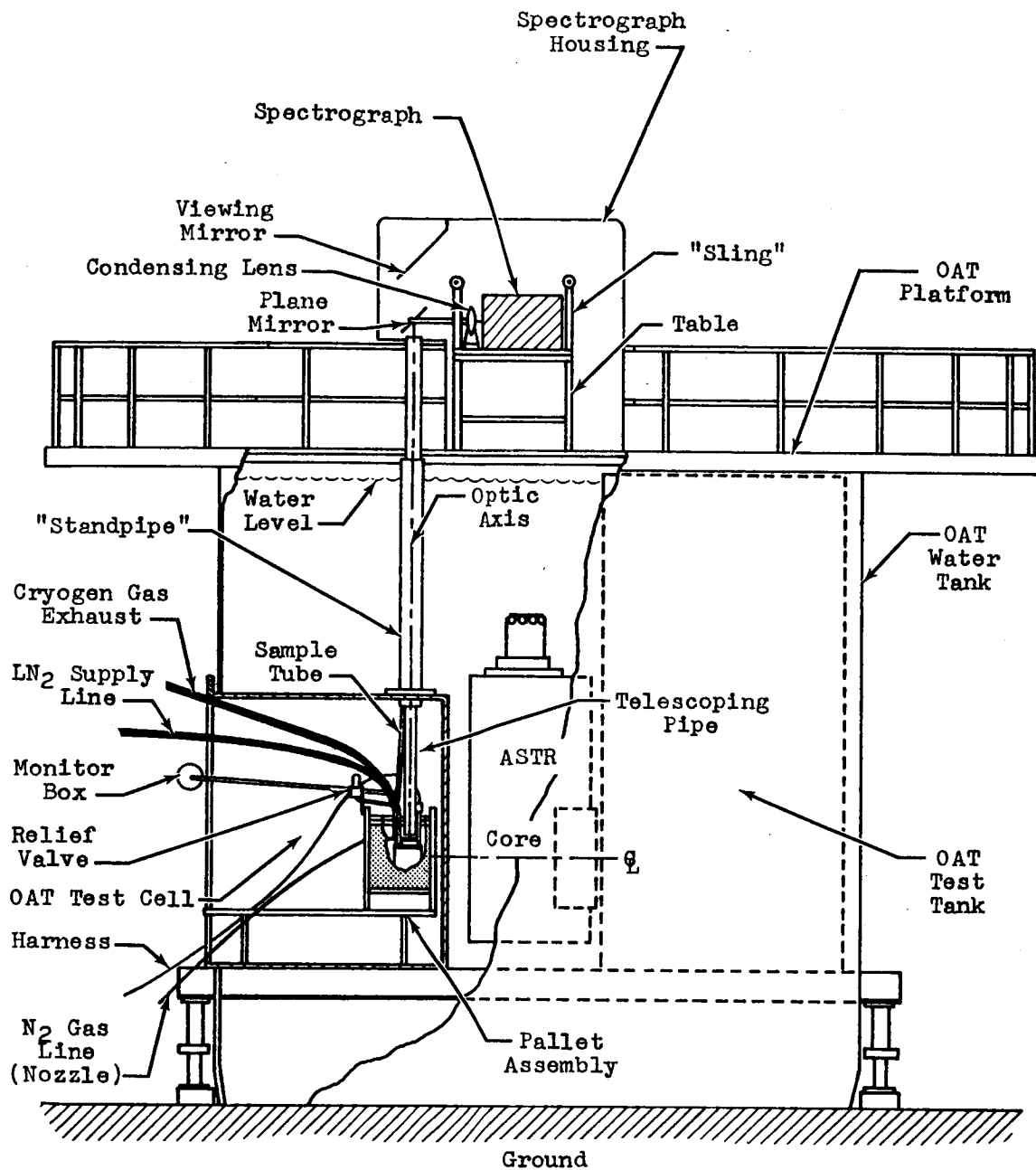


Figure 22 Experimental Arrangement: Closed-Dewar Experiments

LN₂ from a 6500-gal LN₂ storage tank located in another part of the NARF area. A television camera monitored the pressure gages on the tanks (Fig. 23). Control of the LN₂ pneumatically operated supply valve was accomplished by manual control of a Bristol recorder-controller mounted in the radiation-effects console. The solenoid-operated LOX valve was controlled by a switch on this same console. Another regulator in the control room supplied nitrogen gas through a copper line to a nozzle mounted at the edge of the dewar viewing window. This nozzle directed a steady flow of nearly ambient gas on the top of the window to prevent condensation on the area of the window exposed to air (Fig. 21).

The cryogen liquid level in the dewar was monitored by the four resistors in the resistor probe and the eight thermocouples. The resistance changes triggered lights on the liquid-level instrument mounted in the radiation-effects console in the control room. All the thermocouples were fed into a series of Bristol recorders with a range of from +100° to -450° F; the temperature was monitored on a dial and recorded on chart paper. Provisions were also made to select each of the eight thermocouples separately on the Rubicon potentiometer for more precise measurement of the temperature of the cryogenic liquid mixture of LN₂ and LOX at any one of these specific points. The locations of the thermocouple and resistor levels in the dewar are shown in Figure 24. The eight thermocouples

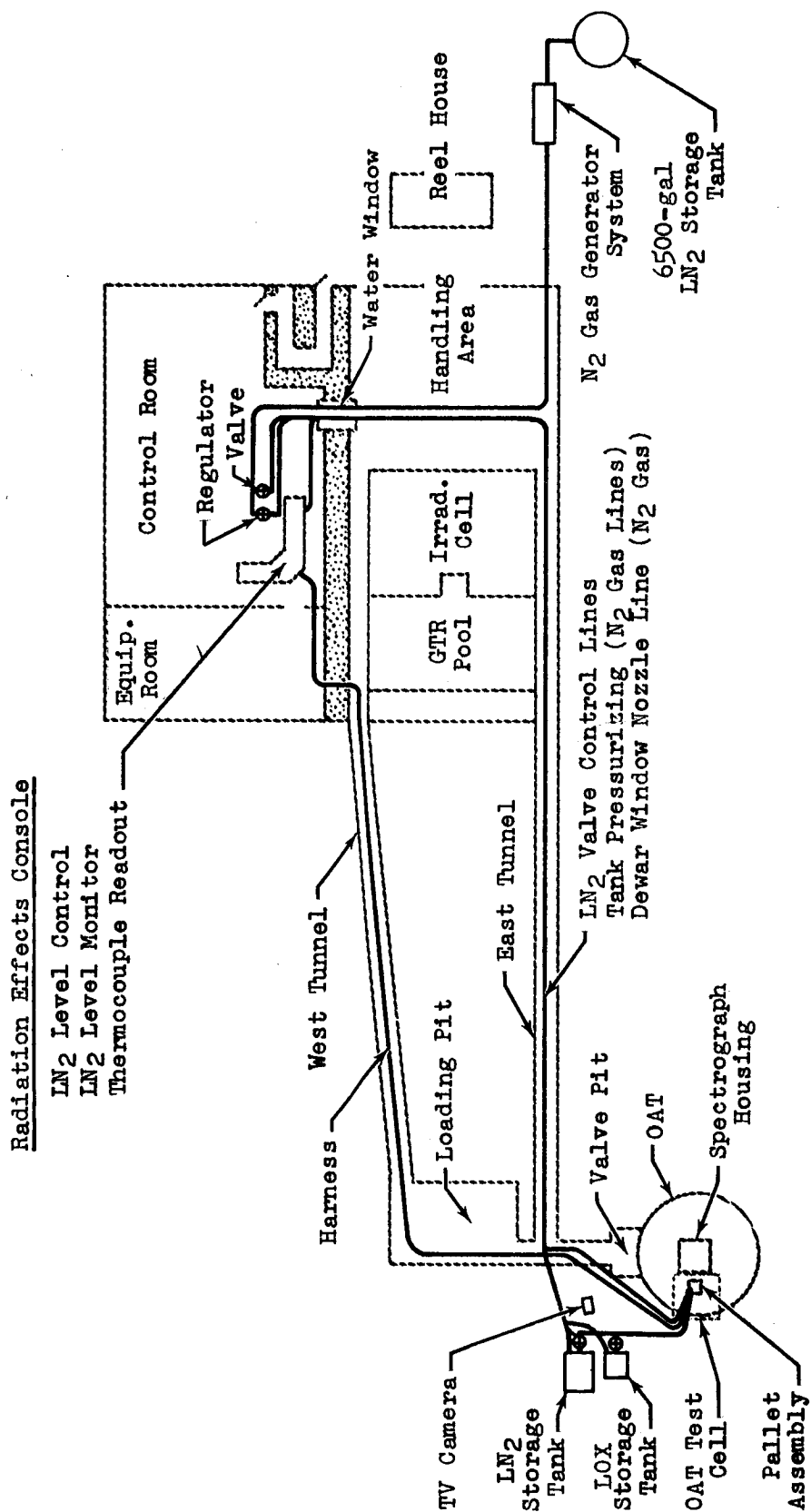


Figure 23 Accessory Equipment: Closed-Dewar Experiments

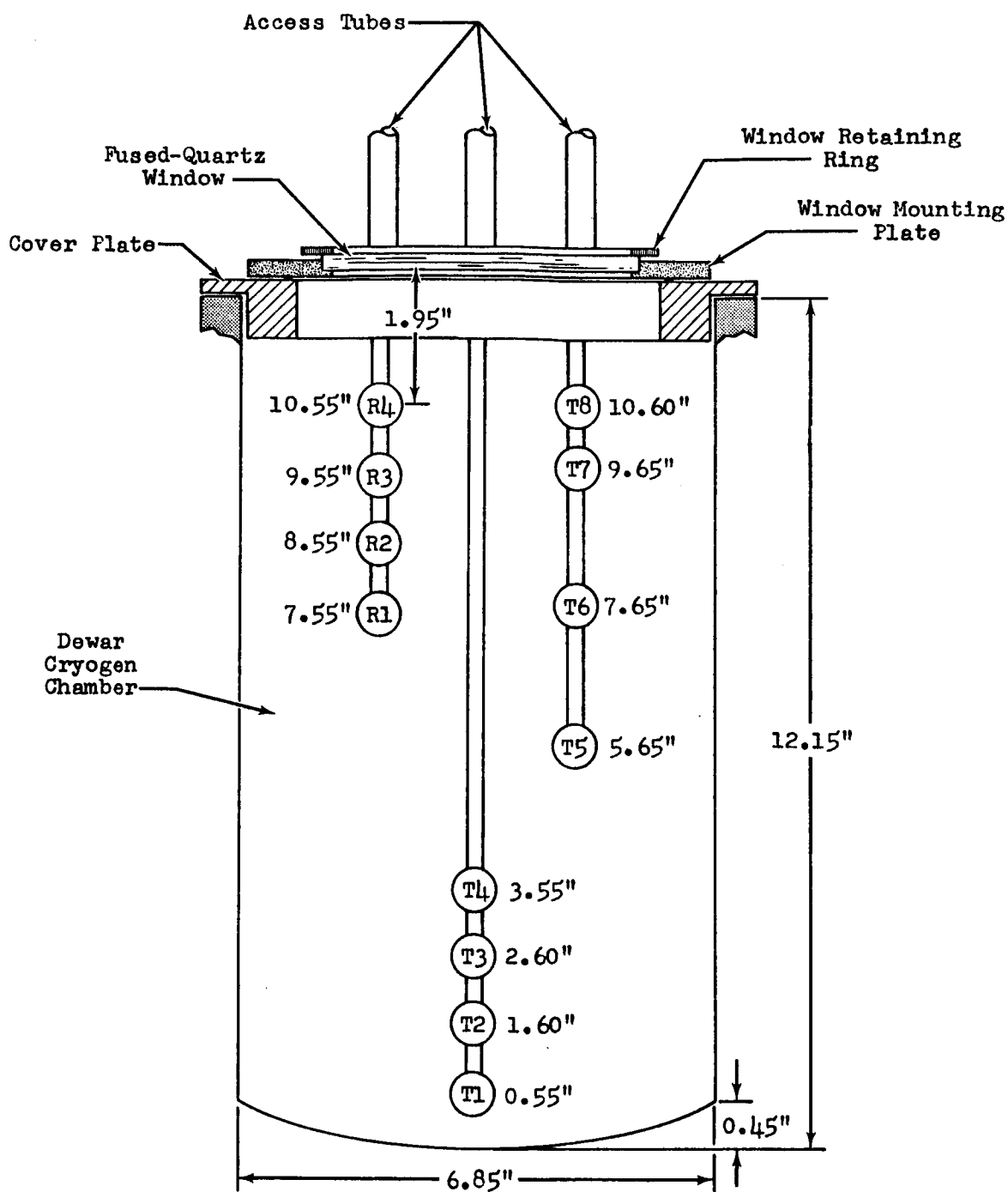


Figure 24. Resistor and Thermocouple Positions: Closed-Dewar Experiments

on the probe were calibrated before the experiment on the Rubicon potentiometer at LOX and LN_2 temperatures against a reference thermocouple in an LN_2 bath. A number of attempts were made to obtain successive temperature readings of mixture percentages of LOX in LN_2 , but the results were somewhat erratic.

The spectrograph employed in the closed-dewar experiments was the Jarrell-Ash Model 75-000 high-dispersion (20 Å/mm at $\lambda 4358$ Å), high-resolution, large-aperture (f/6.3), plane-grating spectrograph with regular plateholder and Polaroid camera attachment. The matching condensing lens and front surface (aluminum) mirror of the open-dewar experiments were also used for the closed-dewar experiments.

In using the test cell of the OAT for these experiments, a telescoping "standpipe" was constructed to provide a light pipe from the slit of the spectrograph, through the water tank and top of the OAT test cell, to within an inch of the dewar window. This arrangement provided a closed path for viewing the bottom of the dewar cryogen chamber and minimized the entrance of stray light into the spectrograph.

4.5.2 Test Procedures

The dewar-pallet assembly containing the closed dewar was set in place at the irradiation site in the test cell of the OAT, where it remained throughout the entire experiment (Fig. 22). Connections were made for the cryogen fill line, cryogen-gas exhaust, relief valve, sample tube, monitor box,

thermocouple, and resistor probe harnesses. About a half hour before the start of the irradiation, the dewar cryogen chamber (Fig. 24) was filled to level position T3 (1.37 liters) with LOX supplied remotely from the 50-gal tank. Then LN_2 was added (remotely supplied) to bring the liquid level up to position R2 (4.94 liters) and afford the liquid mixture a concentration of approximately 27% LOX by volume.

The reactor was then raised and brought up to power at 5 Mw at 0929, September 9, for an irradiation run that totaled 33.6 Mw-hr, with reactor shutdown occurring at 1615. During this time the liquid level in the dewar was maintained between R2 and R3 (Fig. 24) by the addition of LN_2 only. Upon completion of the irradiation, the LN_2 supply was turned off and the contents of the dewar allowed to begin boiling off. At this point, the spectrograph and accessories were to be placed in position on top of the OAT catwalk by crane for viewing the dewar while the boil-off continued.

4.5.3 Test Results and Conclusions

This experiment produced no detectable self-induced explosions during the irradiation period. There was, however, one incident at 1545 (30 minutes before reactor shutdown) of a barely audible sound that seemed to come from the area of the dewar, but it could not definitely be attributed to an actual explosion.

Continuous observation of the instrumentation during

this experiment appeared to indicate that liquid oxygen was being lost from the mixture in the dewar during a period before reactor startup to a few minutes afterwards. Data taken on the temperature as registered by the thermocouples in contact with the liquid in the cryogen chamber of the dewar during the test are given in Table 2. Plots of temperature vs time of two representative thermocouples, T1 and T3, are shown in Figure 25. These plots show the temperature of the liquid approaching that of LN_2 temperature, although it leveled off at -195°C , where it remained until reactor shutdown. At this point, the temperature of the liquid shifted quickly, finally reaching LN_2 temperature. Certain conclusions are drawn from these temperature readings. Apparently, very nearly all the liquid oxygen had been lost by about 1000. The -195°C reading by the thermocouples up to reactor shutdown, instead of -195.8°C (LN_2 temp), can be attributed to gamma radiation heating in the thermocouple.

The reasons for the loss of possibly all the liquid oxygen in the LN_2 and LOX mixture cannot be fully explained. It is believed, however, that the situation in this case was probably similar to that in the first open-dewar experiment, i.e., condition of 2-phase flow must have existed during the somewhat interrupted filling operations, even with the use of much shorter supply lines and lower supply tank pressures. This conceivably effected a boil-off of the mixture, in part,

Table 2

CALCULATED TEMPERATURES FROM RUBICON DATA: EXPERIMENT 4

Time	Thermocouple Locations*							
	T1 (°C)	T2 (°C)	T3 (°C)	T4 (°C)	T5 (°C)	T6 (°C)	T7 (°C)	T8 (°C)
9-9-64								
0930	-194.4	-194.3	-194.7	-194.3	-194.8	-194.7		out of liquid
1000	-194.9	-194.8	-195.0	-195.1	-195.4	-195.3		
1030	-195.3	-195.2	-195.4	-195.1	-195.5	-195.3		
1100	-194.9	-194.7	-195.1	-194.8	-195.2	-195.2		
1130	-194.8	-194.6	-195.1	-194.8	-195.1	-195.1		
1200	-194.9	-194.8	-195.2	-194.9	-195.2	-195.1		
1230	-194.9	-194.8	-195.1	-194.6	-195.1	-195.0		
1300	-194.8	-194.6	-195.0	-194.9	-195.2	-195.0		
1330	-194.8	-194.2	-195.1	-194.7	-195.0	-194.7		
1400	-194.7	-194.6	-195.0	-194.6	-194.9	-195.0		
1430	-194.8	-194.7	-195.1	-194.7	-195.1	-195.1		
1500	-194.7	-194.7	-195.0	-194.7	-195.1	-195.0		
1530	-194.7	-194.7	-195.1	-194.8	-195.1	-195.2		
1600	-194.9	-194.9	-195.1	-194.8	-195.2	-195.2		
1615	-195.0	-194.9	-195.2	-194.9	-195.1	-195.2		
1620	-194.8	-195.1	-195.4	-195.5	-195.9	-195.9		
1630	-195.7	-195.5	-195.8	-195.6	-196.0	-195.2		
1700	-195.7	-195.5	-195.8	-195.7	-195.9	-195.9		
1715	-195.7	-195.6	-195.8	-195.7	-196.5	-195.6		
1730	-195.6	-195.5	-195.8	-195.7	-195.6			
1800	-195.7	-195.6	-195.7	-195.7				
1830	-195.6	-195.5	-195.6	-195.5				
1900	-195.5	-195.6	-195.6	-195.5				

*Refer to Figure 24

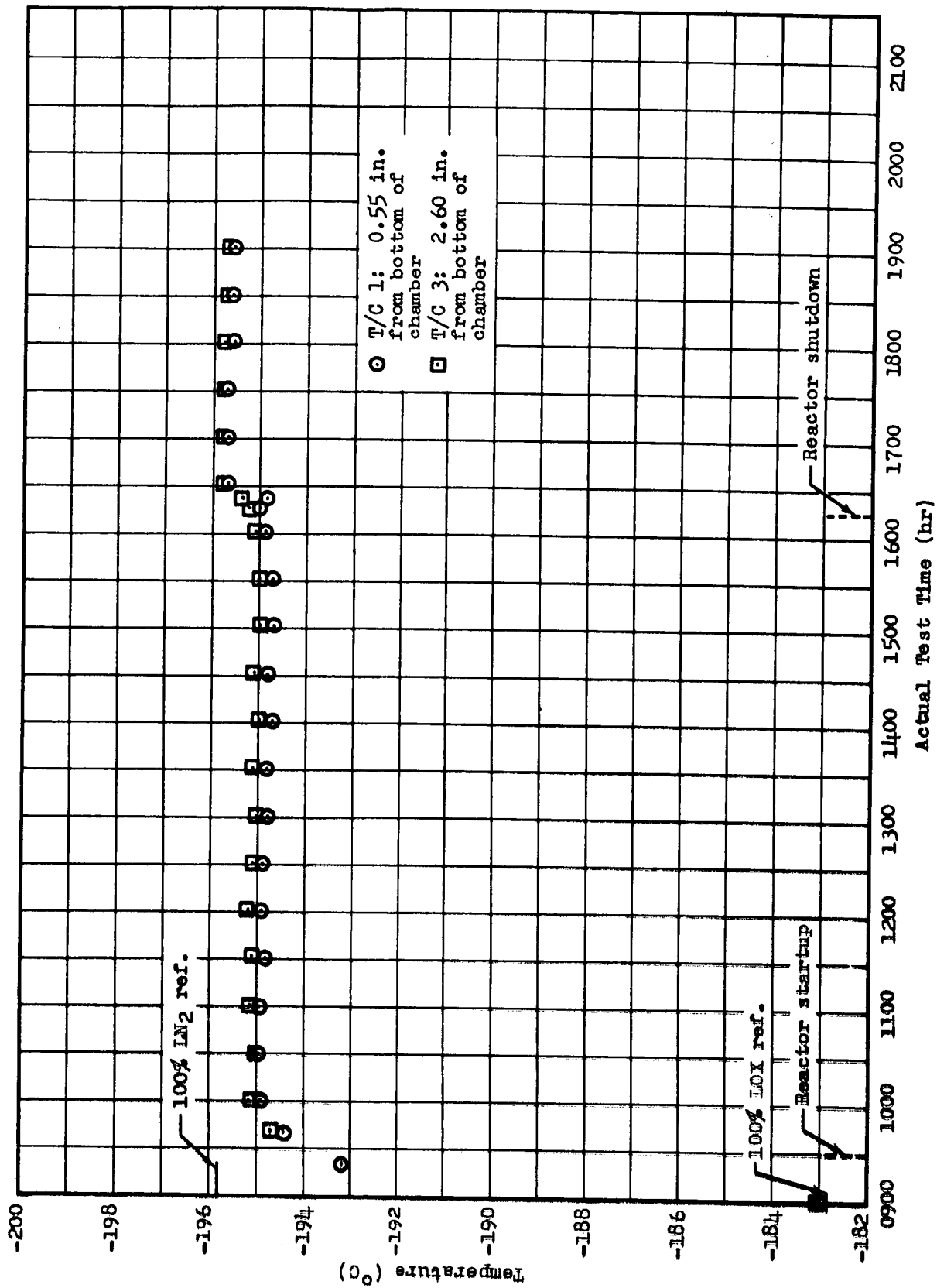


Figure 25 Cryogen-Chamber Liquid Temperature vs Actual Test Time: Experiment 4

when LN_2 was added in an attempt to raise the liquid level in the dewar. Boil-off of LOX in a predominately LN_2 mixture under static conditions should be very minimal because of the lower boiling point of LN_2 , so that only the LN_2 is considered to be boiling off to any significant degree. As a result of the above, it was decided that in the next experiment a nearly constant "trickle" of LN_2 would be maintained during the course of the test. This operating procedure should keep the supply lines close to LN_2 temperature through most of the experiment, thus minimizing 2-phase flow.

In face of the possible oxygen decrease during this experiment, plans were still made to set up the spectrograph and accessory equipment after reactor shutdown to monitor the dewar spectrographically in case an explosion ensued. Numerous difficulties were experienced, however, in relocating the spectrograph from the planned location of the equipment, because of very high radiation background present even an hour after the irradiation. This was attributed mainly to back-scattering arising from the stacks of concrete shielding at the opening of the test cell.

With the dewar cryogen chamber level (which had been dropping during the relocation of the spectrographic equipment) now reaching a critical point (about 3 in. above the bottom of the chamber), a decision was made to attempt to increase the level of the liquid by adding LN_2 to the dewar. This

attempt was made in spite of the risk involved in this refilling procedure, because of the possibility of introducing 2-phase flow, especially through the previously warmed-up supply line, which might accelerate boil-off of the remaining contents of the dewar, as described earlier. The dewar liquid level did drop, before liquid could be added, to a point where T1 just began showing the thermocouple to be out of liquid. At this point, a weak explosion occurred. The LN_2 filling operation was suspended. Observation of all the thermocouples showed them to be rising in temperature more rapidly now, indicating that there was no more liquid left in the dewar. The low level of the audible sound led to the speculation that, had the spectrograph been in place and the dewar allowed to boil off normally, the products formed by the irradiation of the mixture would not have produced an explosion with sufficient intensity to permit spectrographic recording of this event.

Examination of the dewar after the experiment showed no damage to the cryogen chamber of the probes. The fused-quartz window, however, showed discoloration in many areas as a result of irradiation. These areas showed up as various shades of purple in planes or streaks throughout clear sections of the fused-quartz window. Measurements of transmissivity vs wavelength of the window viewing area by the Perkin-Elmer Model DK-2 spectrophotometer indicated that the loss in transmission of the irradiated fused-quartz window amounted to 50% over

a large portion of the visible area. However, the planned use of the Polaroid ASA 10,000 film instead of the ASA 3,000 film used in this experiment would have compensated for this decreased transmission. (An EPR study of the irradiated window is given in Section 5.2.4.)

4.6 Experiment 5: Closed-Dewar Test (16 September 1964)

4.6.1 Test-Equipment Description

The equipment incorporated in Experiment 5 was the same as that used for the first closed-dewar experiment, except for a new fused-quartz window, which replaced the window used previously in Experiment 4.

The eight thermocouples were recalibrated against the reference thermocouple (in LN_2 bath) at LOX and LN_2 temperatures to determine whether any change in the previous calibration had taken place in the thermocouples as a result of irradiation during the previous test. There was no apparent change in calibration.

Attempts were made again to read the liquid temperature of various mixtures of LOX and LN_2 in the IML before this experiment. Several runs using different methods of preparing the mixtures were made, and these runs appeared to provide some consistency in the data. These data are plotted in Figure 26 as temperature vs percentage of oxygen in the mixture.

4.6.2 Test Procedure

The dewar-pallet assembly was placed in the OAT test

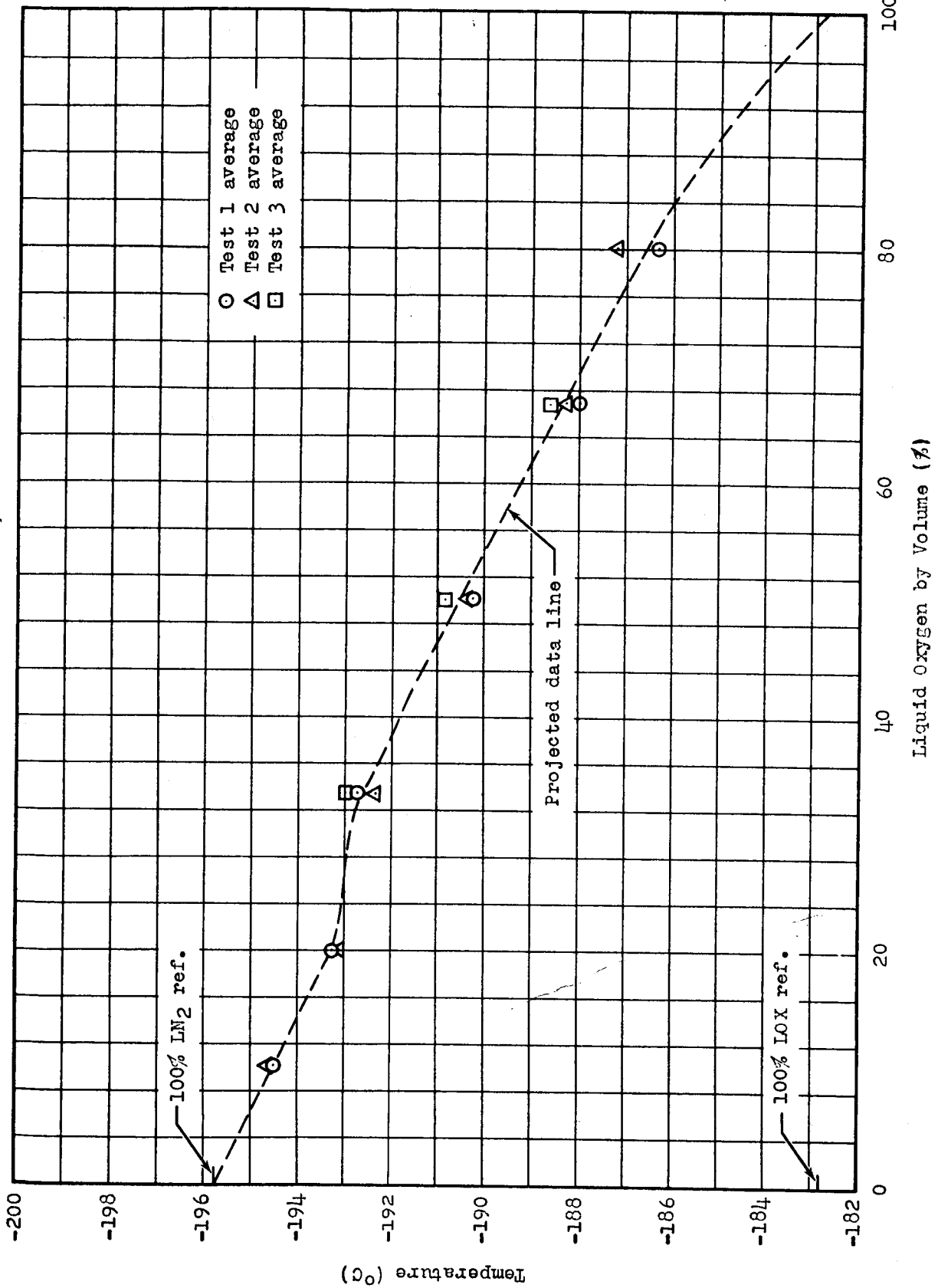


Figure 26 Cryogen Liquid-Mixture Temperature vs Liquid Oxygen by Volume: Laboratory Experiment

cell at the irradiation site, with the various equipment and lines being attached to the dewar as in the foregoing experiment (Fig. 22).

At 1015 on September 16, LN_2 was supplied to the dewar and the liquid level was brought up to T_4 , which corresponded to an amount of 1.94 liters of LN_2 in the dewar (Fig. 24). After the dewar was allowed to pre-cool for a few minutes, the LN_2 level was brought back to this point (T_4) at 1030; then LOX was supplied to the dewar to bring the level of the liquid mixture up to R_2 , which corresponded to an addition of 3.1 liters of LOX to the dewar.

The reactor was raised into position and brought to a power of 6 Mw at 1207. The power level was raised to 7 Mw at 1639 for the remaining period of the run, with reactor shutdown occurring at 1830 after 40-Mw-hr.

The spectrograph and associated equipment were moved into the new position on top of the OAT test tank after the radiation background level had subsided somewhat. The spectrograph was ready to record with the camera loaded at 2115, at which time the background level had dropped to about 100 mr/hr.

4.6.3 Test Results and Conclusions

This experiment produced no definitely detectable self-induced explosions. There were a few barely audible sounds, however, that did appear to come from the vicinity of the dewar during the period of the irradiation portion of the

experiment. However, it is surmised that these sounds could have been "static" picked up by the audio system.

The temperatures recorded by the thermocouples during this experiment appeared to show in the loss of oxygen a trend which was similar to that observed in the first closed-dewar experiment. Part of the decrease in the oxygen concentration was occurring while the liquid level was being held between R1 and R2 (Fig. 24) by the addition of the LN_2 to the dewar in a continuous "trickle" flow. This constant flow condition was obtained at 1215, just after reactor startup. Before this time, an interrupted flow was necessary because of the very-slow liquid boil-off rate occurring with no reactor heating of the dewar.

Data taken on the temperature of the thermocouples in contact with the liquid during the test are given in Table 3. A plot of temperature as a function of time of representative thermocouples T1 and T3 is shown in Figure 27. This plot shows the liquid temperature at about -188°C at 1100, which from Figure 26, is about a 70% oxygen mixture by volume. The liquid level in the dewar was just below T6 at the time, indicating that nearly all the oxygen added earlier was still in the dewar. At 1130, however, a 45% oxygen mixture was indicated by the thermocouples; and, at reactor startup, the oxygen concentration was down to 12% by volume of the mixture in the dewar.

Table 3

CALCULATED TEMPERATURES FROM RUBICON DATA: EXPERIMENT 5

Time	Thermocouple Locations*							
	T1 (°C)	T2 (°C)	T3 (°C)	T4 (°C)	T5 (°C)	T6 (°C)	T7 (°C)	T8 (°C)
9-16-64								
1100	-187.6	-188.5	-188.2	-188.1	-188.6	-188.5		
1130	-192.0	-193.1	-193.5	-193.2	-193.7	-193.6		
1200	-193.9	-194.4	-194.4	-194.4	-194.7	-194.6		
1230	-193.1	-193.5	-193.5	-193.1	-193.7	-193.7		
1300	-193.8	-193.9	-194.1	-194.0	-194.4	-194.4		
1330	-194.7	-194.7	-195.0	-194.6	-194.8	-194.8		
1400	-194.8	-194.9	-195.1	-194.8	-195.2	-195.1		
1430	-194.8	-194.9	-195.1	-194.7	-195.2	-195.2		
1500	-194.9	-194.9	-195.2	-194.7	-195.1	-194.9		
1610	-194.9	-194.9	-195.1	-194.7	-195.0	-194.9		
1730	-194.9	-194.9	-195.2	-194.8	-195.2	-195.1		
1825	-193.9	-193.9	-194.1	-193.9	-193.8	-194.2		
1845	-195.8	-195.8	-196.9	-195.8	-195.8	-195.7		
1900	-196.0	-195.9	-196.1	-195.8	-195.8	-195.7		
1920	-196.1	-196.0	-196.1	-195.9	-195.9			
2000	-196.0	-196.0	-196.1	-195.9	-195.8			
2100	-195.9	-196.0	-196.0	-195.9	-195.9			
2145	-195.9	-195.9	-195.9	-195.9	-195.9			
2215	-195.8	-195.9	-195.8	-195.9	-195.8			
2235	-195.7	-195.7	-195.8	-195.9	-195.8			
2245	-195.6	-195.6	-195.8	-195.9	-195.8			
2250	-195.3	-195.3	-195.8	-195.9	-195.8			
2255	-195.0	-195.0	-195.8	-195.9	-195.8			
2300	-194.8	-194.8	-195.8	-195.9	-195.8			
2305	-194.2	-194.2	-195.8	-195.9	-195.8			
2310	-192.5	-195.9	-195.8	-195.9	-195.8			
							out of liquid	

*Refer to Figure 24

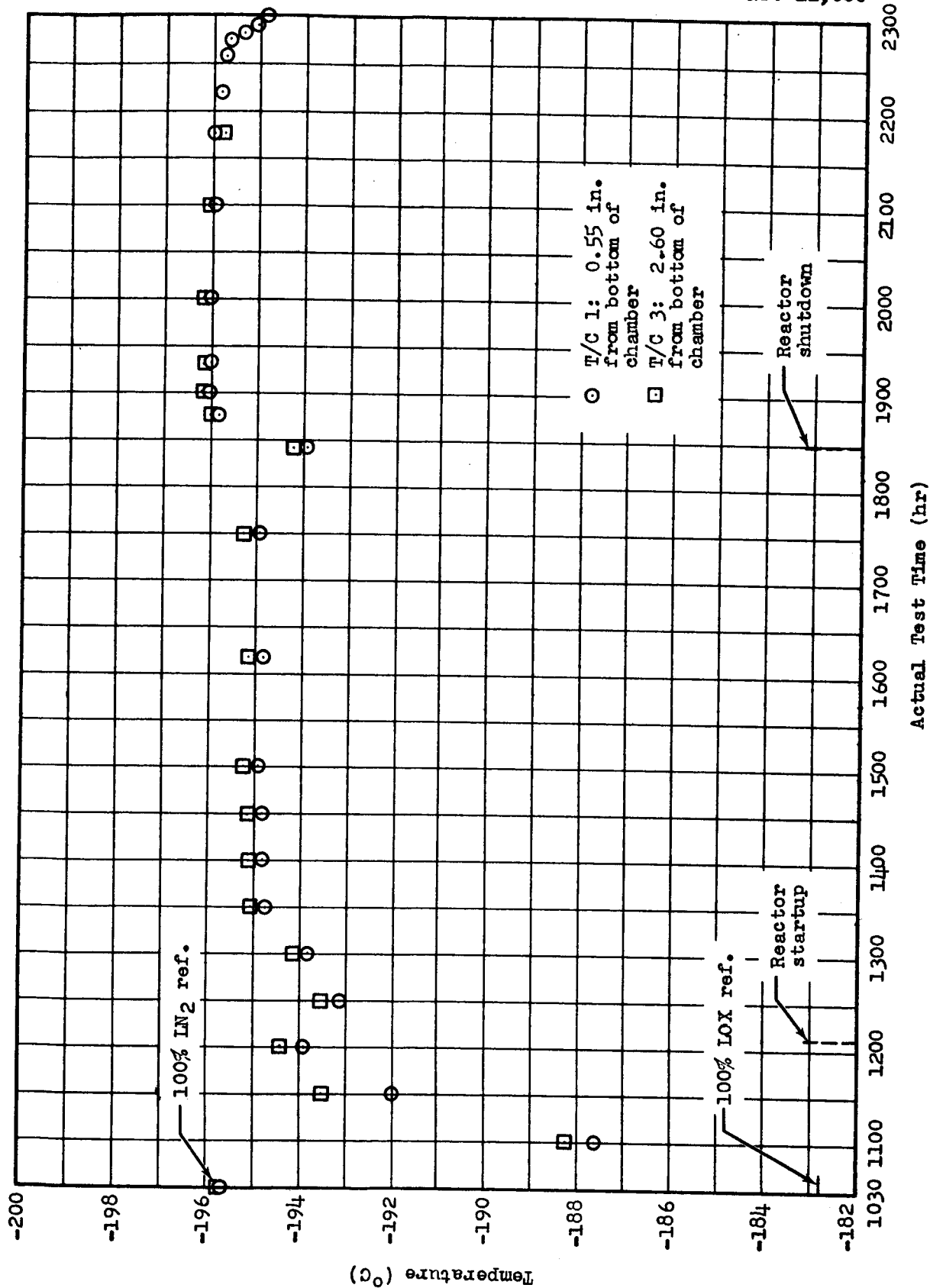


Figure 27 Cryogen-Chamber Liquid Temperature vs Actual Test Time: Experiment 5

After reactor startup, there was a shift in the temperature due to radiation heating of the thermocouples. The oxygen content of the mixture still continued to decrease for another two hours after reactor startup (under steady LN_2 flow conditions), but at a slower rate, to a point at 1400 where the temperature leveled off at -195°C , as in the fourth experiment. Soon after reactor shutdown, the thermocouples assumed a value nearly (no reactor heating) that of the temperature of LN_2 (-195.8°C). This seems to verify the fact that loss of nearly all the oxygen was experienced very early in the period of the irradiation of the dewar. The unusual readings by the thermocouples at 1825 cannot be explained. The recording equipment appeared to be operating satisfactorily when rechecked.

It was decided during the course of the experiment that no additional oxygen would be supplied to the dewar to replace that which the instrumentation lost. The possibility of greater concentrations of oxygen in the dewar going undetected and being irradiated had more oxygen been added could have placed the experiment above a safe operating condition. It was concluded that more research into controlling and measuring cryogenic mixtures by the use of thermocouple techniques needs to be conducted to provide greater reliability in this method.

No explosions were obtained after reactor shutdown during the entire boil-off period of the irradiated liquid in the dewar. A plot of the rate of boil-off in the dewar during

this test is shown in Figure 28. Thus attempts to record emission spectra by exposing photographic film in the spectrograph trained on the closed dewar were frustrated. During the $2\frac{1}{2}$ -hr exposure period, eight exposures were made with ASA 10,000 film; in all cases the developed film showed only slight fogging due to background radioactivity and "stray" light.

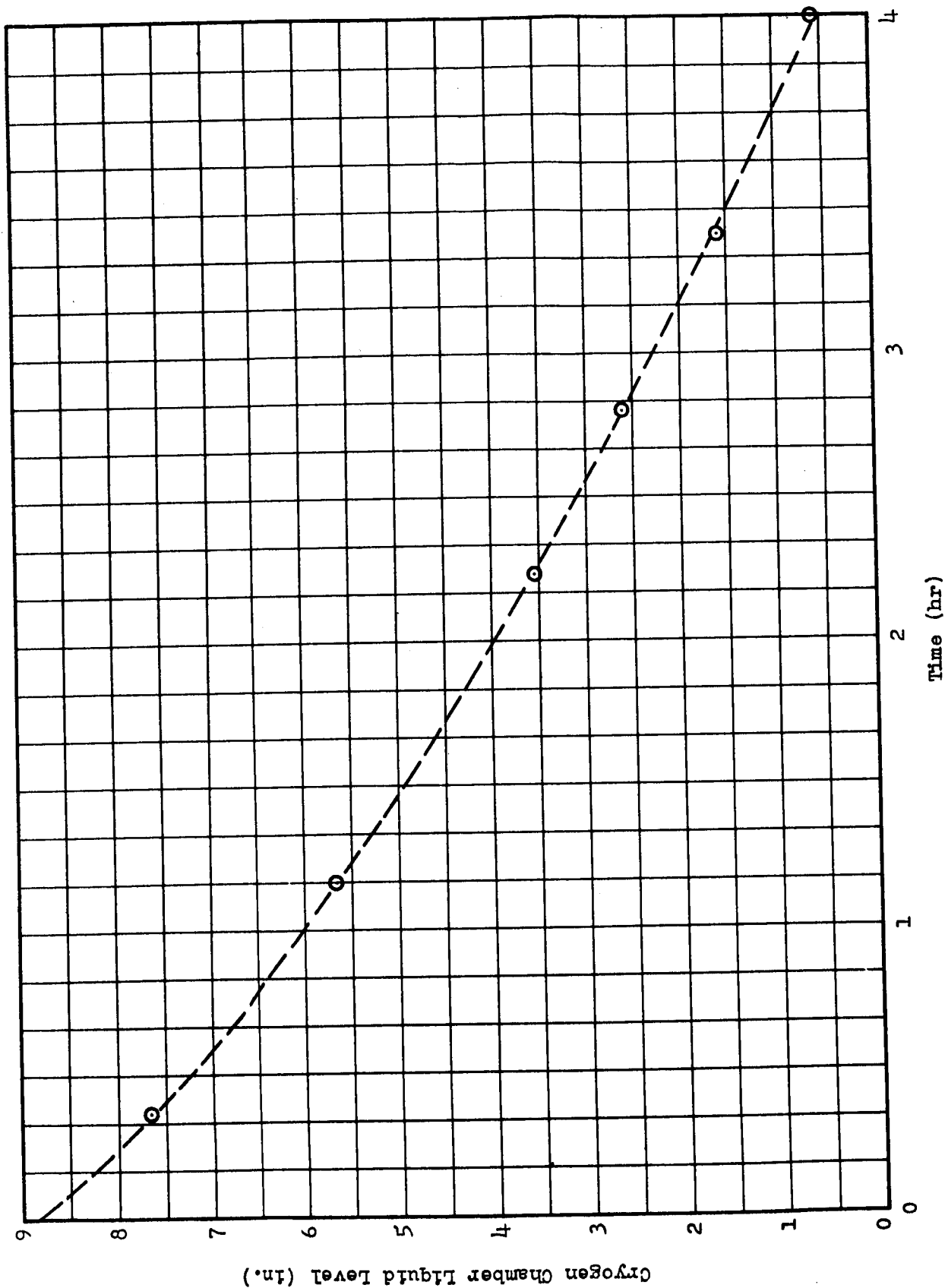


Figure 28 Cryogen Boil-Off Rate: Experiment 5

V. EPR SPECTROSCOPY OF IRRADIATED IMPURE LIQUID NITROGEN

5.1 Technical Discussion

5.1.1 Introduction

Paramagnetic substances have been investigated by a number of methods, chief of which are the measurement of susceptibility and paramagnetic rotation, together with the microwave frequency technique of electron paramagnetic resonance (EPR). EPR spectroscopy has the advantage that each paramagnetic species in a given sample displays its own spectrum, which is different from those of other types. Accurate information can be obtained even for very small quantities of a material.

The use of EPR techniques in the investigation of free radicals is based on the existence of magnetic fields set up by the spins of unpaired electrons. Associated with the spin-angular momentum of the electron \underline{S} is a magnetic moment $\underline{\mu}$ given by the relation $\underline{\mu} = -g\beta\underline{S}$, where for a free electron, g , the gyromagnetic ratio, is 2.0023; β , the Bohr magneton, is 0.92732×10^{-20} erg/gauss; and the magnitude of spin angular momentum \underline{S} is $\pm 1/2$.

In a uniform magnetic field of strength \underline{H} , the electron spin \underline{S} precesses about the direction of \underline{H} with the Larmor frequency $\nu = (g\beta/h)H$, where h is Planck's constant, 6.623×10^{-27} erg-sec. The electrons may possess either of two precessional energies, given by $-\underline{\mu} \cdot \underline{H} = \pm 1/2 g\beta H$. If electro-

magnetic energy is put into the system at the Larmor frequency ν with the magnetic vector perpendicular to \underline{H} , then electrons in the lower state may be raised to a higher state through the resonance absorption of an amount of energy equal to $h\nu = g\beta H$.

Such resonance absorption is ordinarily observed by holding the frequency of the microwaves constant and modulating the strength of the uniform magnetic field at a relatively slow rate (from audio frequencies up to 100 kc). Then an observed resonance absorption of electromagnetic energy at a strength H implies a characteristic "splitting constant" (line separation) of $\nu = g\beta H/h$, which provides, among other things, a means of identifying the free radicals in a sample material. Using microwaves of wavelength 3.2 cm, it is found that for free electrons $\nu = 9368.4$ Mc/sec and $H = 3342.8$ gauss (Ref. 29). Definite variations in these values are observed for unpaired electrons associated with different molecules and with different excited states of the same molecule (Ref. 30).

Two important problems are encountered in EPR studies of paramagnetic liquids: the broadening of the resonance absorption peak due to the effect of "Brownian tumbling" and the effective decrease in microwave absorption due to "saturation." These two effects correspond to opposite situations. Broadening occurs when the relaxation time of orientational electronic states is so short that the uncertainty in resonance absorption

energy is large. Saturation occurs when the relaxation time is so large that the absorption of microwave energy results in a steadily increasing "spin temperature" leading ultimately to a condition in which no further energy is absorbed. The relaxation time T_2 depends upon a number of different effects, the most important of which have been treated theoretically (Ref. 31). The line widths are related to the total relaxation time T_2 by the relation $\Delta\nu \sim 1/(2\pi T_2)$. Broadening is a problem when $\Delta\nu$ is almost of the order of ν . Saturation is a problem when T_2 is long compared to time spent in raising the energy states of a significant fraction of the electrons.

In the application at NARF, some of the paramagnetic species under investigation at LN_2 temperature are in the liquid state, e.g., O_2 and O_3 ; others are solids at 77°K , e.g., NO and NO_2 .

5.1.2 Paramagnetism of Molecules in Irradiated Impure Liquid Nitrogen

The radiation chemistry of liquid nitrogen has been the subject of some conflicting reports, as discussed in Section 5.1.1. Some investigators have reported that explosions are caused by ozone which is formed from traces of oxygen in the nitrogen; others indicate that ozone is not formed but that the oxides of nitrogen are responsible for these explosions. It is the purpose of the EPR studies to investigate the formation and decay of paramagnetic species in X-irradiated samples of impure

LN₂ in order to obtain an understanding of some of the basic mechanisms leading to these explosions. A review of the extent of the paramagnetism of the various species expected in irradiated impure LN₂ is outlined below.

Oxygen. Molecular oxygen has an even number of electrons, but two of these remain unpaired and, as a consequence, gaseous oxygen is strongly paramagnetic. Liquid oxygen is also paramagnetic and its susceptibility, χ , follows the Weiss law, namely $\chi = C/(T + \Delta)$, where T is the temperature in °K, and C is constant for a given paramagnet. Perrier and Onnes have reported that the term Δ varies with the concentration of oxygen in liquid nitrogen from 2.2° for 8.1% O₂, to 29.5° for 74.6% O₂ (Ref. 32).

Ozone. Ozone has been the subject of some very conflicting reports in the literature. The molecule has an even number of electrons, and there is no reason for expecting it to be like O₂. Laine has done the most impressive work on O₃ so far (Ref. 33). His measurements indicate that the molar susceptibility of pure liquid O₃ is $0.14 (\pm 0.02) \times 10^{-6}$, which is very small. Gaseous O₃ seems to be diamagnetic.

Nitric Oxide. Nitric oxide in the gaseous phase is paramagnetic. At low temperatures, NO dimerizes to N₂O₂, which is diamagnetic. Bizette reports that the susceptibility of the liquid at 100°K is only 3.52×10^{-6} and shows that this could be interpreted as proving 97% association to N₂O₂ (Ref. 34). Lips finds that solid NO has a very feeble paramagnetism (Ref. 35).

is used to detect and record the sample resonances. A special quartz dewar is used with the multipurpose EPR cavity for studying samples at the temperature of LN_2 . Slots in the cavity wall permit simultaneous irradiation and resonance detection studies. Auxiliary equipment includes a frequency meter, a detector, and a microwave power meter, to measure the microwave power and frequency ν ; a proton resonance gaussmeter and electronic counter were used to measure the magnetic field H .

As stated previously, EPR spectral data on these paramagnetic molecules are not available in the literature; hence the NARF approach has been to investigate the spectra of these species first and then to search for these species in irradiated solutions of LN_2 -LOX. More detail is given in the following sections.

5.2.2 Resonance Spectra of Expected Paramagnetic Species

The paramagnetic species expected to be present at 77°K in irradiated solutions of LN_2 and LOX are O_2 , NO , NO_2 , and O_3 . Of these, NO and NO_2 should be frozen (solid state), whereas O_2 and O_3 should remain in the liquid state. The melting-point and boiling-point temperatures of the various molecular species are given in Table 4. It is noted, therefore, that pure O_3 should be a solid at 77°K ; however, with as much as 0.5% impurity, the melting point of ozone is lowered by approximately 10°K (Ref. 42), so that under these conditions the ozone formed will not solidify. Furthermore, in the amount

Nitrogen Dioxide. Like NO, NO₂ has an odd number of electrons. Havens, on the basis of his gaseous susceptibility measurements at 20°C, has reported that the moment for nitrogen dioxide corresponds to one unpaired electron spin (Ref. 36). No information was found on NO₂ in the liquid or solid state.

5.1.3 Survey of the EPR Studies of O₂, O₃, NO, and NO₂

The EPR spectra of gaseous O₂ and NO have been observed by Beringer and Castle (Refs. 37 and 38). A large number of component lines have been found, and these have been fitted to the theoretical pattern with a good degree of accuracy. The paramagnetic resonance spectrum of gaseous NO₂ has also been observed by Castle and Beringer (Ref. 39). Bird, Baird, and Williams have examined the spectra of solutions of NO₂ in CCl₄ and in CS₂ at room temperatures (Ref. 40). Lin has discussed the calculation of energy levels of paramagnetic molecules in the gaseous state and in dilute solution (Ref. 41). However, nothing on the EPR spectra of these paramagnetic species at liquid-nitrogen temperature was found in the literature.

5.2 Experimental Program

5.2.1 Introduction

The molecular species O₂, NO, NO₂, and possibly O₃ are paramagnetic and, under the proper conditions, they can be studied by EPR techniques.

The Varian V-4500 100-kc EPR spectrometer and 12-in. magnet system are used for these studies. The spectrometer

that ozone is formed in irradiated impure LN_2 , ozone will be completely miscible in the system: $\text{N}_2 - \text{O}_2 - \text{O}_3$ (Ref. 43).

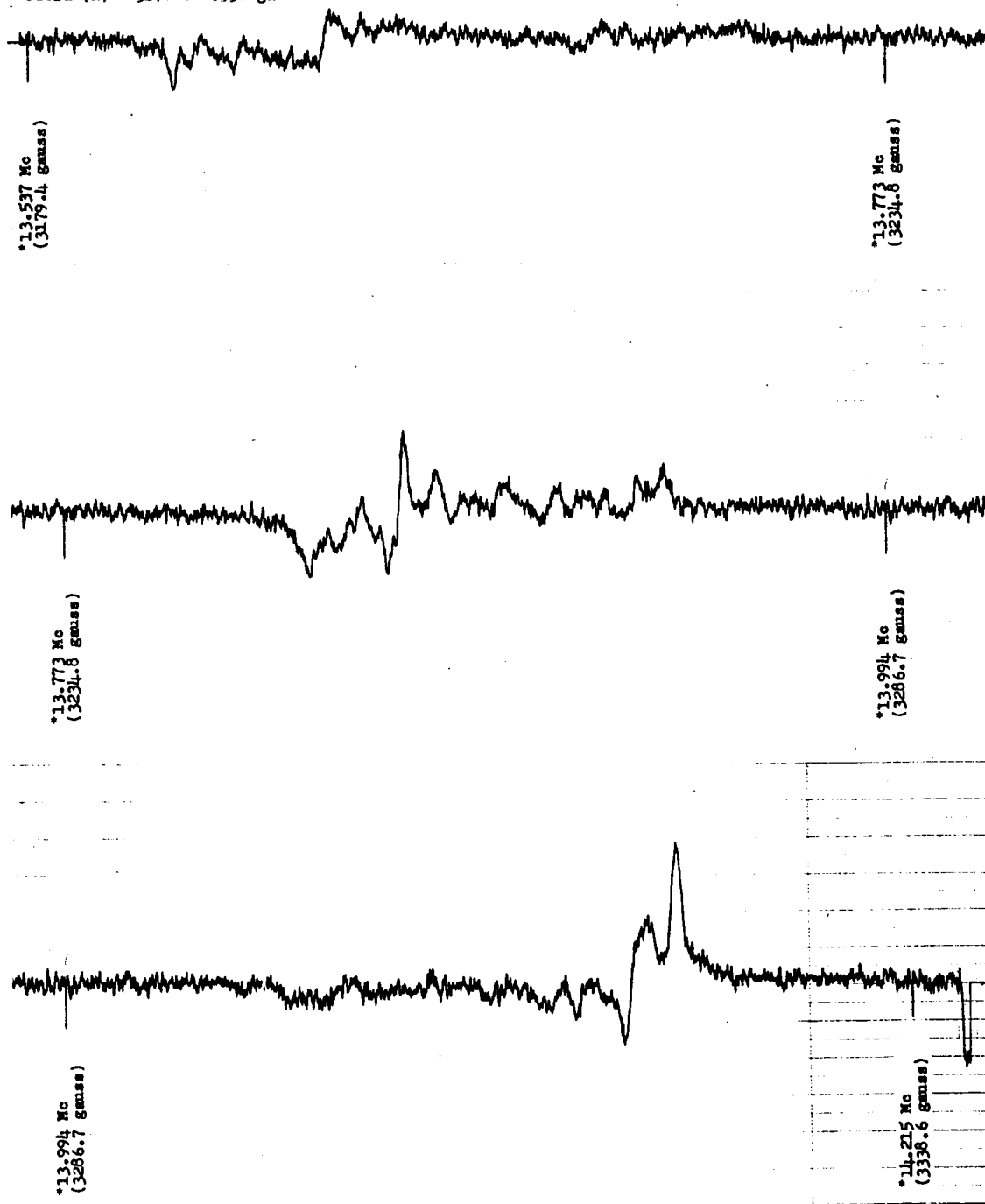
Table 4
MELTING AND BOILING POINT TEMPERATURES

Molecule	M.P., $^{\circ}\text{K}$	B.P., $^{\circ}\text{K}$
N_2	63.3	77.4
O_2	54.8	90.2
O_3	81.1	161.3
NO	109.6	121.4
NO_2	263.9	294.5

Attempts have been made at the IML at NARF, GD/FW, to obtain EPR data on each of these species. The results are discussed below.

Nitrogen Dioxide. An EPR spectrum (first derivative) of NO_2 in LN_2 at 77°K obtained in this study is shown in Figure 29. Bottled NO_2 , obtained from the Matheson Company, Inc., was used in the experiment. The NO_2 gas was condensed in a pyrex tube immersed in LN_2 , and frozen at 77°K . The pellet that was formed was transferred to the quartz LN_2 dewar, which, together with the LN_2 and the NO_2 pellet, was mounted in the microwave cavity. Scanning of the magnetic field revealed an EPR spectrum consisting of three major lines. The g values of these three lines were found to be $g_1 = 1.963$, $g_2 = 2.003$,

Power 5.5 mw
 Mod. Ampl. 0.3 gauss
 Sig. Level 1600
 Response 0.3 sec
 Freq. (ν) 9.125 gc
 Field (H) 3179 to 3339 gauss



Note: Continuous strip-chart recording divided into three sections, with overlap

*Frequency of proton-resonance gaussmeter

Figure 29 EPR Spectrum (First Derivative) of NO_2 in LN_2

and $g_3 = 2.039$, as calculated from the relation $g = h\nu / \beta H_0$. The microwave frequency was 9.125 gc.

Several NO_2 spectra were obtained, with some variations observed in the different spectra. The most striking difference was observed after a 90° rotation of the LN_2 dewar containing the NO_2 pellet. The resonance spectrum of the rotated NO_2 pellet is shown in Figure 30.

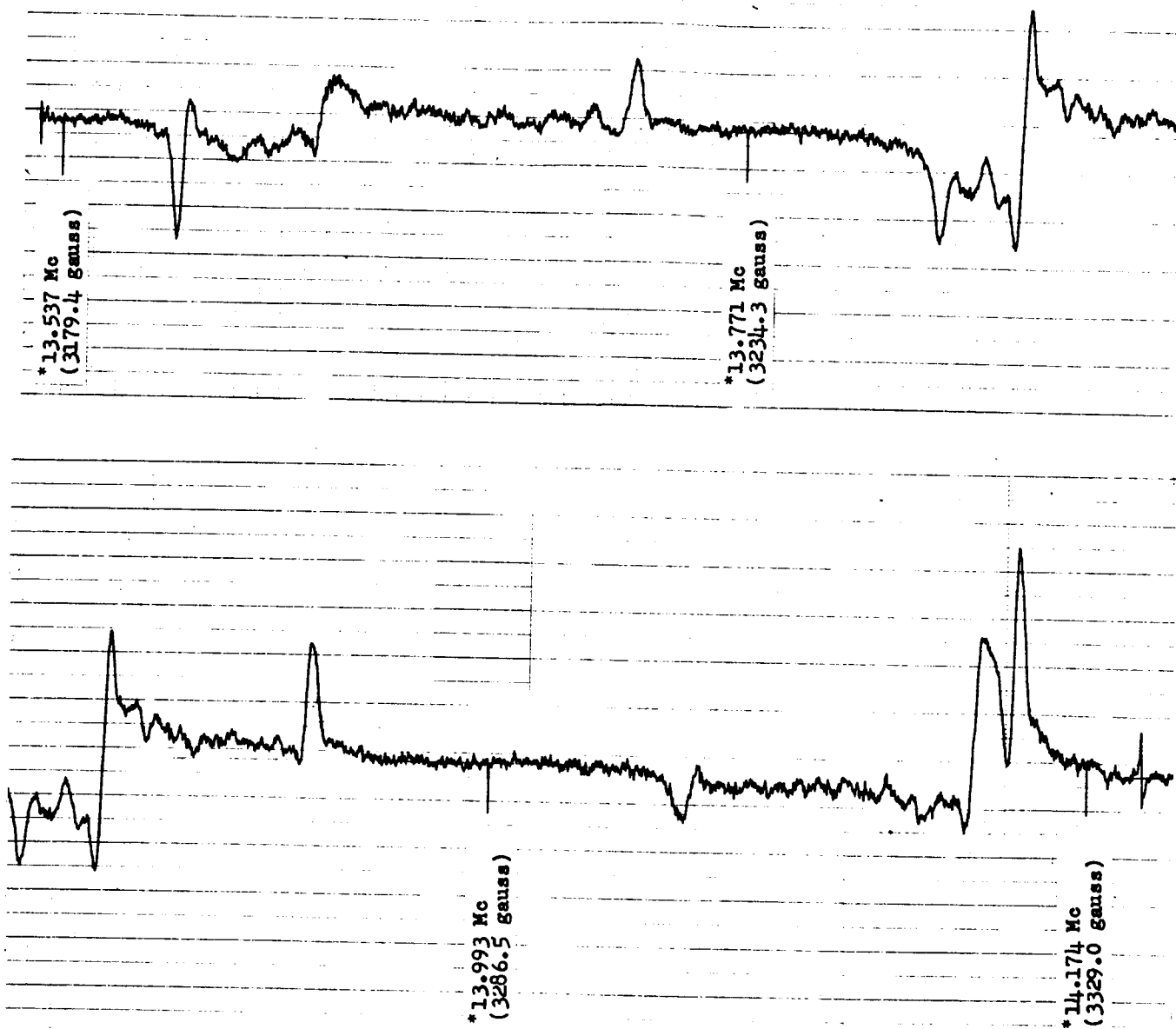
Prior to the NO_2 pellet transfer technique, an unsuccessful attempt was made to obtain the resonance spectrum of an NO_2 sample which was condensed and frozen in a quartz sample tube. The tube and sample were then placed in the LN_2 dewar, which was positioned in the cavity for resonance detection. (The NO_2 and LN_2 were not in contact.) No resonances were detected, however; the reduced sample size and additional quartz could have reduced the signal-to-noise ratio so that the signal was probably lost in the noise.

One major factor which influences the detection of NO_2 is the equilibrium concentration of NO_2 at low temperatures. At low temperatures, the nonparamagnetic species, N_2O_4 , is formed according to the relation $2\text{NO}_2 \longrightarrow \text{N}_2\text{O}_4$. This may account for the relatively weak resonance detected in the frozen NO_2 sample.

Additional data on NO_2 is needed in order to establish better g values and to determine the spectral variation as a function of orientation of the NO_2 crystal with respect

Power 17.5 mw
Mod. Ampl. 0.7 gauss
Sig. Level 1000

Response 0.3 sec
Freq. (ν) 9.125 gc
Field (H) 3179 to 3329 gauss



Note: Continuous strip-chart recording divided into two sections, with overlap

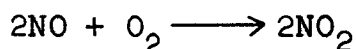
*Frequency of proton-resonance gaussmeter

Figure 30 EPR Spectrum (First Derivative) of NO_2 in LN_2 : Rotated Sample

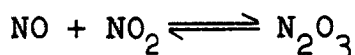
to the applied magnetic field.

Nitric Oxide. Pellets formed by condensing and freezing NO gas have been examined for resonances at 77°K in the EPR spectrometer using the LN₂ dewar apparatus. Weak resonance peaks were obtained, however; the g values corresponded to those for NO₂ in LN₂ (77°K).

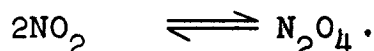
A possible explanation for this is that oxygen present in the transfer line and in LN₂ leads to the reaction



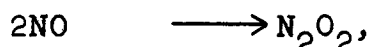
and, at low temperatures, to these reactions:



and



Another reaction, indicated earlier, is



and N₂O₂ is not paramagnetic. These reactions would reduce the concentration of the paramagnetic species NO and NO₂. Additional data on NO are needed for identification of the molecule in the presence of other paramagnetic species. The use of an improved transfer system for condensing and freezing NO gas will preclude, or at least minimize, oxidation of NO. This will enhance the probability of obtaining better EPR spectra.

Oxygen and Ozone. Preliminary runs have been made on O₂ in LN₂ and on O₃ and O₂ in LN₂. Liquid oxygen was obtained both as LOX and by condensing gaseous O₂ at 77°K. The O₃-O₂

mixture was obtained by passing gaseous O_2 through an ozonizer having a conversion efficiency on the order of a few percent. The ozonizer supplied the energy necessary for the reaction $3O_2 \longrightarrow 2O_3$ to take place. The gas mixture was condensed and then transferred to the LN_2 dewar. Of the numerous runs made on liquid O_2 and O_3 , no resonances were detected. These preliminary runs were made in order to develop and improve the techniques of sample preparation and observation of the primitive resonances.

In the case of liquid O_2 , some oxygen molecules dimerize at low temperature (77° to $113^\circ K$) to form O_4 molecules. The O_4 dimer is believed to exist partly in a diamagnetic singlet state and partly in a paramagnetic form, and the susceptibility is small compared to the large paramagnetic susceptibility of gaseous oxygen (Ref. 43). This would make it difficult to interpret EPR data on liquid O_2 .

Ozone is believed to be only very weakly paramagnetic, as discussed previously; hence further attempts to observe this species should be made on samples of higher ozone concentration.

5.2.3 X-Irradiation of LN_2 -LOX Solutions

Experimental Techniques. Several different methods were considered for the irradiation and observation of small volumes of the LN_2 -LOX solutions by EPR techniques. These methods incorporated a quartz capsule, external irradiation of the

solution with liquid transfer to the dewar, and in situ irradiation of the loaded dewar.

In addition to providing only a small irradiation volume, the use of a quartz capsule containing LN_2 -LOX solutions presented fabrication and containment problems. Furthermore, irradiated quartz exhibits strong resonances which would complicate interpretation of the data.

The irradiation of a loaded dewar external to the spectrometer was considered feasible; however, the irradiation of the quartz dewar would introduce undesirable resonances that might complicate the interpretation of the data. Also, the initial quantity of LN_2 -LOX is small, being limited to approximately 70 ml. By shielding that portion of the dewar which would be located within the microwave cavity and by adding LN_2 -LOX as necessary, the problems could be minimized.

Another method considered in these studies involved the external irradiation of the LN_2 -LOX solution in a large (12-in. x 6-in.-ID) dewar with subsequent transfer of liquid to the quartz dewar used with the spectrometer. Longer irradiation and observation times are possible with the larger reservoir of LN_2 -LOX. The dewar can remain in the cavity and outside the X-ray field. Irradiation and observation can be performed simultaneously. The major problem here is the transfer of a representative sample of the irradiated LN_2 -LOX into the dewar positioned in the microwave cavity.

The in situ irradiation of a loaded quartz dewar involves similar problems. In this instance, the quartz dewar, especially the section within the cavity, would be exposed to the radiation. It is also possible to damage the cavity by X-irradiation. Again, only a small volume is exposed. This in situ configuration, incorporating an external supply dewar, was utilized. LN_2 -LOX was remotely transferred to the quartz dewar as necessary.

Equipment Description. The necessary dewar lid and transfer lines were fabricated for the external X-irradiation of LN_2 -LOX solutions. This external dewar system was used to supply the quartz dewar with the LN_2 -LOX solution for the in situ X-irradiation. The dewar vessel, bracket, and lid are shown in Figure 31. The lid has an aluminum window for transmission of X-rays, fittings for three 1/4-in.-OD lines, a fitting for an 1/8-in.-OD line, and a relief valve. The three larger lines were used for pressurizing, venting, and adding cryogenic fluids. The smaller line is for transfer of liquid to the quartz dewar. The aluminum window is double-walled, forming a chamber with an inlet and outlet in series with the ports for one of the larger lines, and was to be used for irradiation external to the cavity. The arrangement incorporating a separate supply dewar system with in situ X-irradiation of the quartz dewar as described in the previous section was used.

The experimental setup is shown in Figure 32, 33, and 34. The shield on which the X-ray tube is mounted is shown

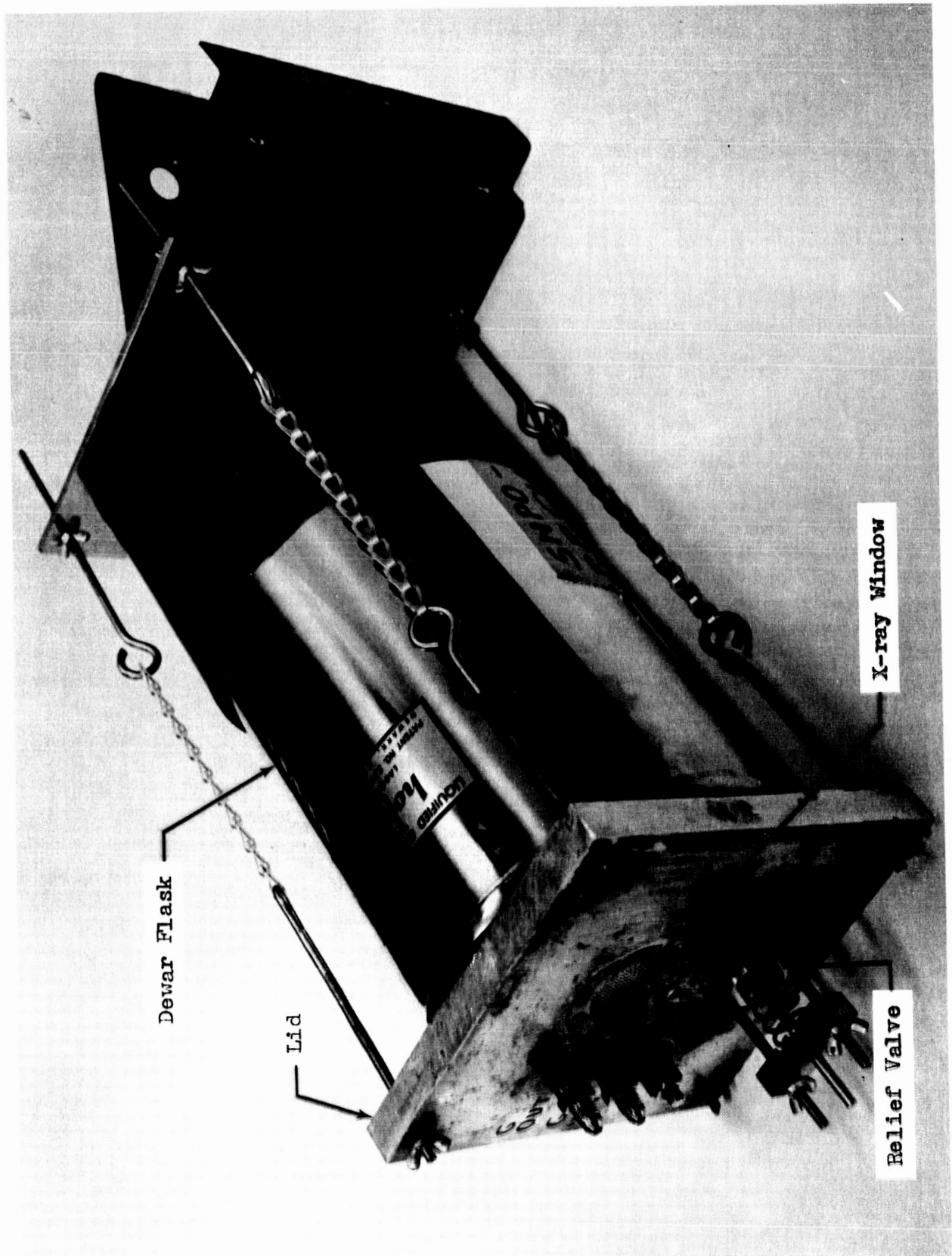


Figure 31 Supply Dewar Assembly

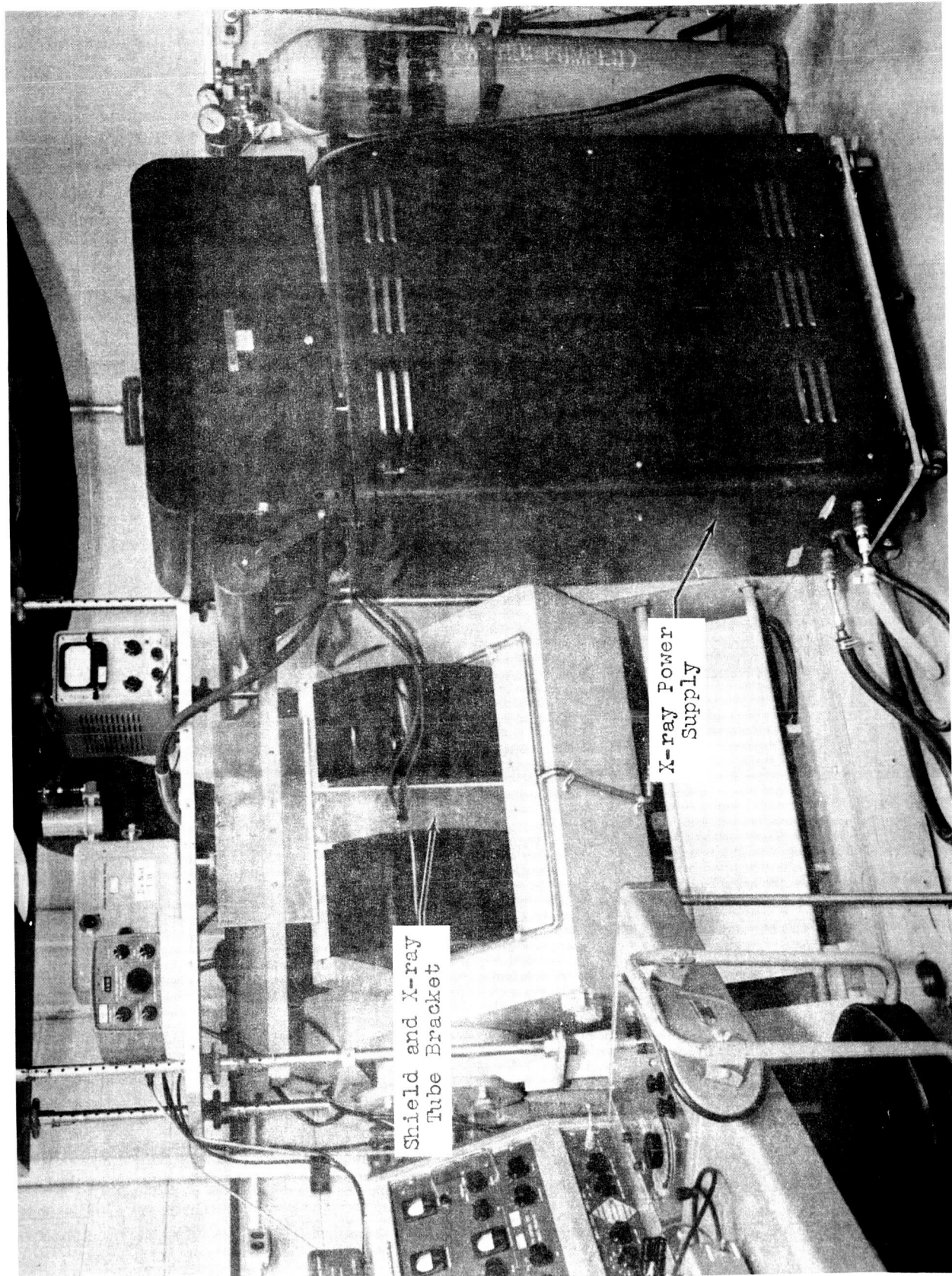


Figure 32 EPR Spectrometer and X-Ray Unit

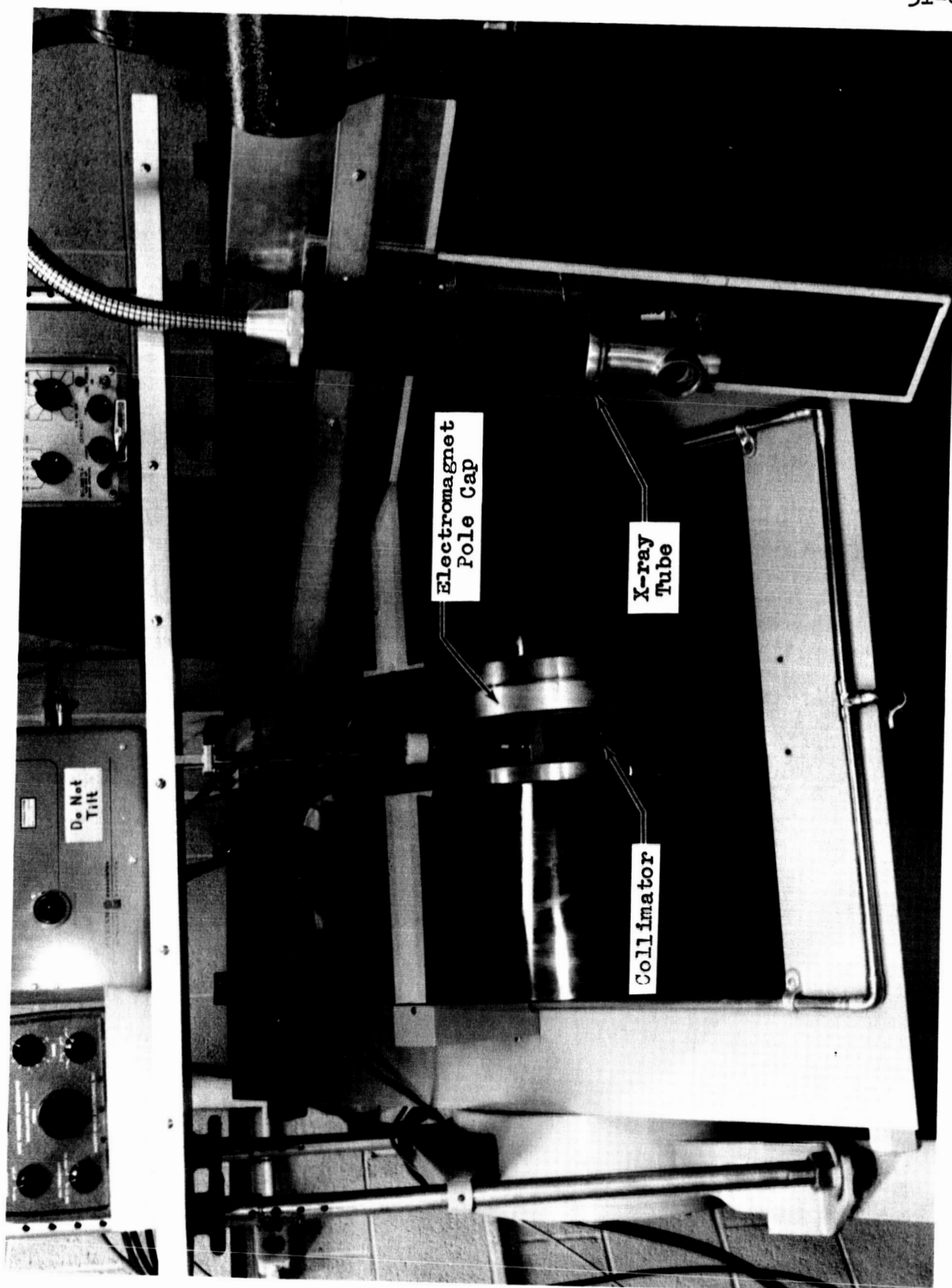


Figure 33 Spectrometer Magnet with X-Ray Tube Removed

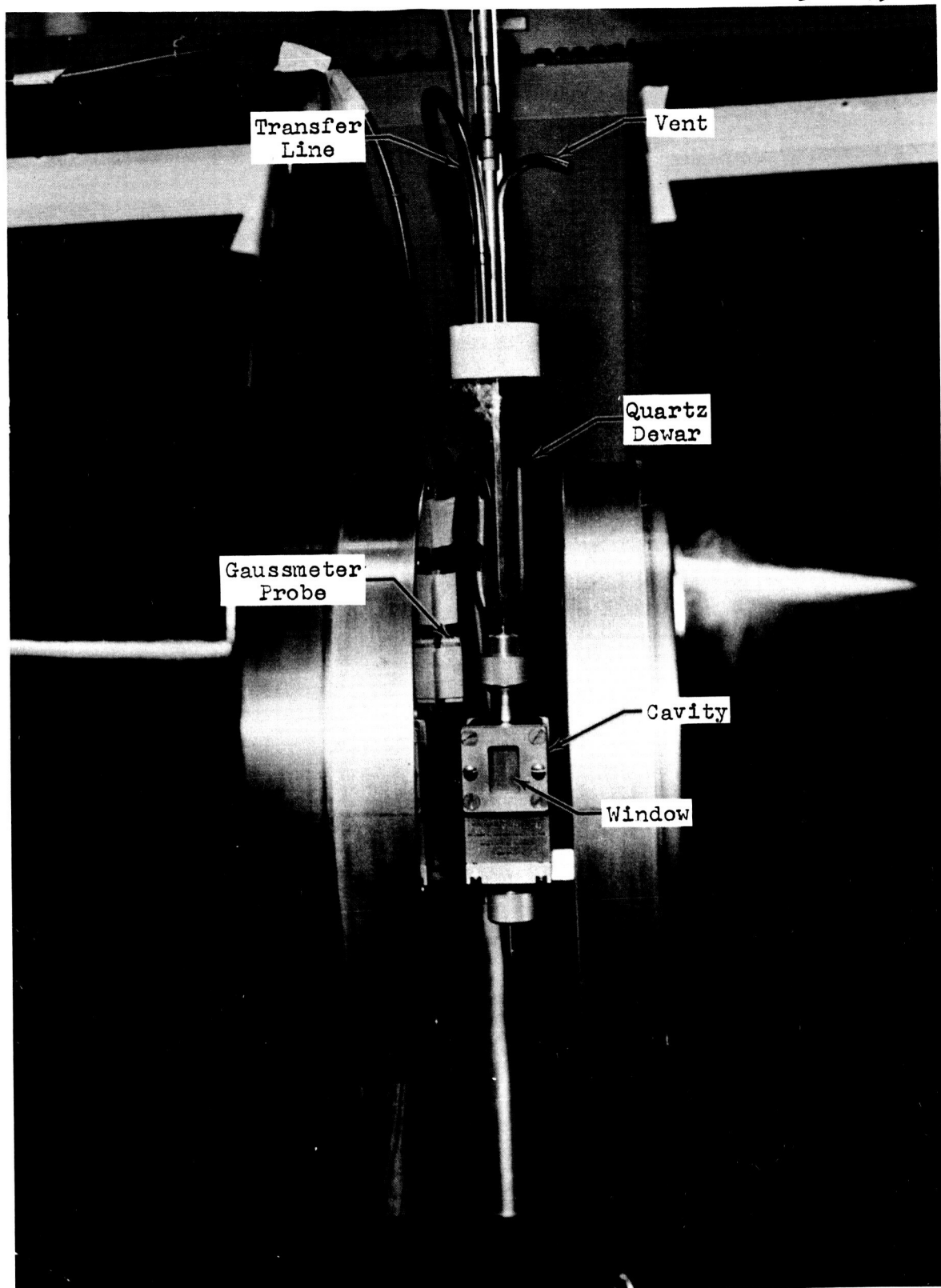


Figure 34 Spectrometer Cavity and Quartz Dewar

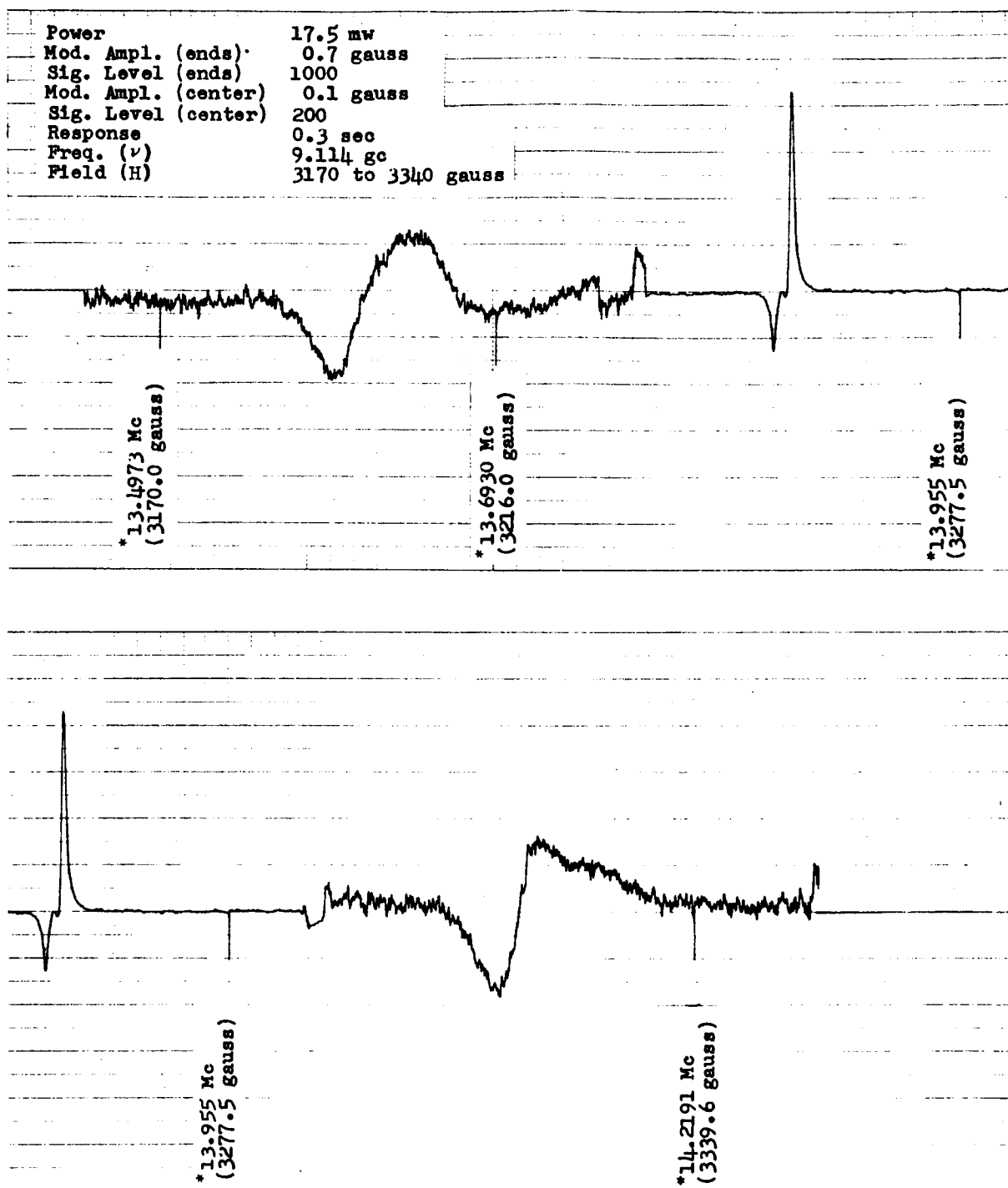
in Figure 32 along with the magnet and 20 kv X-ray power supply. The X-ray tube used is a Type AEG-50 obtained from Machlett Laboratories, Inc. In Figure 33, the shield and the X-ray tube have been removed to show the lead collimator in front of the cavity and between the pole faces. Figure 34 shows the cavity, slotted window to the cavity, and the quartz dewar with transfer lines.

Experimental Results. EPR spectral data were obtained during the in situ X-irradiation of solutions of 10% LOX in LN_2 and 20% LOX in LN_2 in a quartz dewar. Irradiation was accomplished by X-rays from a 20-kv 20-ma tungsten-target X-ray tube. The estimated sample dose rate was approximately 5×10^4 r/hr. The quartz dewar was maintained partially full by remote transfer of the LOX- LN_2 solutions from a separate storage dewar.

Data were obtained on the solutions for magnetic field H from 3090 gauss to 3570 gauss at the microwave frequency, $\nu = 9.1$ gc. No resonances were observed other than those attributed to the irradiated quartz-dewar vessel.

Quartz resonance data were obtained later at room temperatures, as shown in Figure 35. Three distinct quartz resonances were observed at relative g values of 1.9638, 2.0004, and 2.0365, respectively.

The relative g values are estimated to be accurate to within ± 0.0003 ; bias in the g values is considerably greater



Note: Continuous strip-chart recording divided into two sections, with overlap

*Frequency of proton-resonance gaussmeter

Figure 35 EPR Spectrum (First Derivative) of Quartz Sample Dewar

due to difficulty in the absolute measurement of ν and H .

5.2.4 EPR Studies: Experiment 4

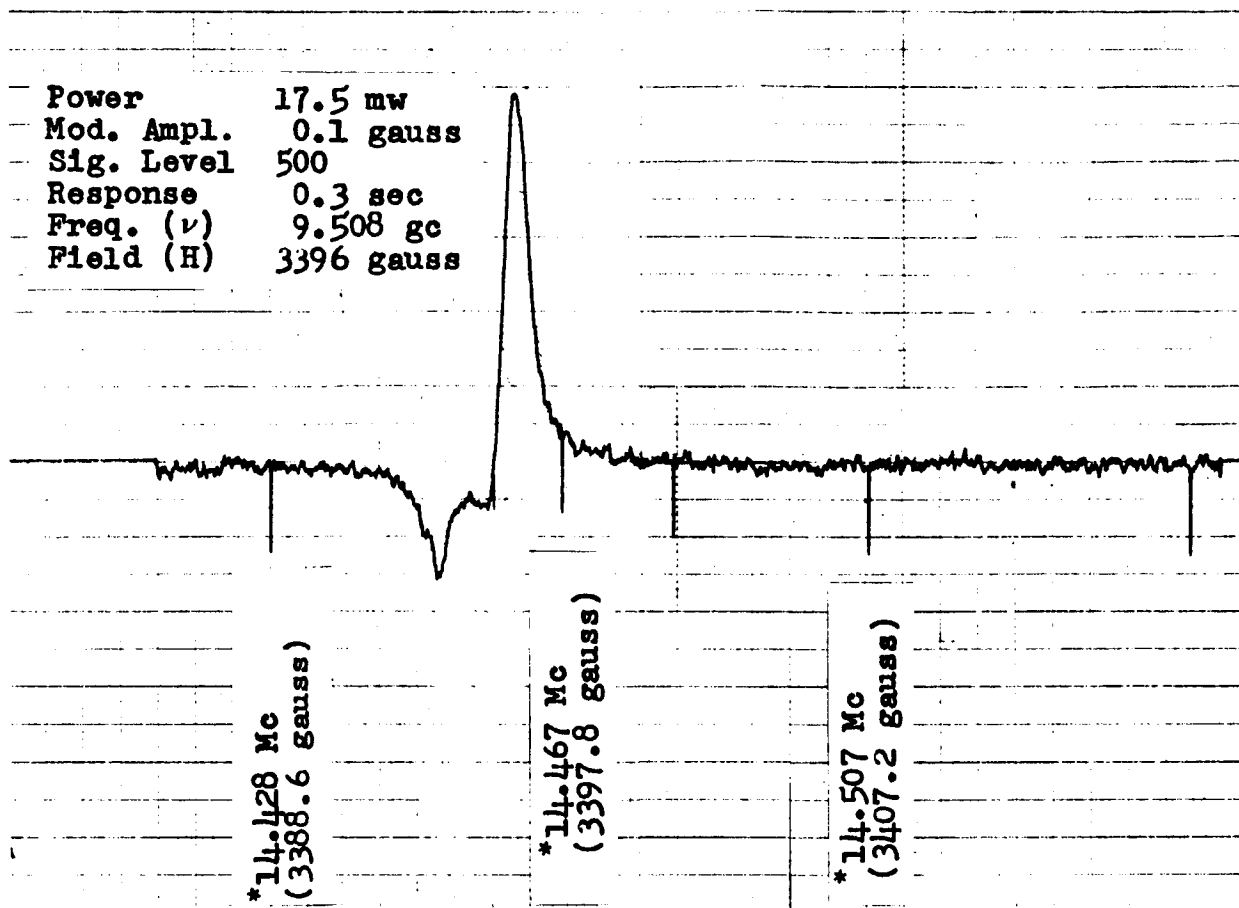
Small sections of an unirradiated and reactor-irradiated quartz window used in Experiment 4 were examined for paramagnetic resonance; none was observed in the unirradiated specimen, whereas a single resonance was detected in the irradiated sample. The trace is shown in Figure 36. The resonance at $g = 2.0004$ (relative value) is, within experimental limits, identical to the prominent resonance obtained by X-irradiation of the quartz spectrometer dewar and is attributed to color centers.

5.3 Conclusions

EPR spectra were obtained of the species NO_2 and NO . In the case of NO_2 , an angular dependent spectrum was obtained. A similar spectrum was observed for NO . These spectra are essential to the study of irradiated impure LN_2 and, to the author's knowledge, the first ones ever to be reported. Further work on these species is desirable using more pure samples to verify the identity of the paramagnetic species and to establish more precise g values.

In the case of O_2 and O_3 in LN_2 , no resonances were observed; however, the experiment is not considered conclusive, and further work is indicated.

In situ studies of X-irradiated solutions of LN_2 -LOX were conducted. The observed EPR spectra were attributed to the



*Frequency of proton-resonance
gaussmeter

Figure 36 EPR Spectrum (First Derivative) of Fused-Quartz Window

color centers in the quartz dewar. Small concentrations of the possible paramagnetic species would give rise to weak and perhaps unobservable spectra that could be easily masked by the strong signal due to color centers in the quartz. Therefore, further studies should be pursued that will exploit: (1) high irradiation doses, to increase the concentration of the paramagnetic species; (2) a larger reservoir of LN_2 -LOX, to obtain a greater yield of paramagnetic species; and (3) irradiation of a sample volume external to the cavity, to avoid the spectrum due to the color centers in quartz.

VI. SUMMARY AND CONCLUSIONS

6.1 Engineering Experiments

Five reactor-irradiation experiments were conducted on dewars containing LN_2 with various amounts of oxygen and other constituents as impurities. The first three experiments involved "open" dewars initially charged with known quantities of LOX, but admitting as impurities into the dewars unknown amounts of water vapor and other condensable constituents of the air, such as O_2 and CO_2 . These were primarily conducted as "preliminary experiments" to obtain data on dewar performance and test techniques to be used in the design of "closed" dewars and experimental procedures therewith. The closed-dewar experiments were designed to yield quantitative data on controlled amounts of irradiated LN_2 containing known amounts of constituents introduced as impurities remotely therein.

As it developed, however, difficulties were experienced in controlling the amounts of cryogenic fluids - both LN_2 and LOX - let into the closed dewars while the nuclear reactor was at power, mainly because of 2-phase flow of the cryogens during filling operations, which was aggravated by gamma-ray heating of the dewar and cryogen inlet tubes. As a result, most of the data obtained in this entire study on explosions per se involved open dewars, in which case the problem of 2-phase flow had been solved satisfactorily with the use of the deceleration dewar. But the fact that these data were

obtained on unknown quantities of condensed impurities under somewhat uncontrolled conditions within the dewars precludes quantitative analysis of the data obtained under this study to date, allowing only qualitative observations and conclusions. Only two closed-dewar experiments were conducted prior to the premature cutoff of this project, at a time when the 2-phase flow problem was being solved.

The experiments conducted in this program lead to several general observations and conclusions. Self-initiated (spontaneous) explosions can occur in irradiated open dewars of LN_2 initially charged with oxygen as an impurity (1) both during the course of irradiation, as observed in Experiments 2 and 3 (E2, E3), and after reactor shutdown but before all the liquid contents have boiled off, as in E2 and weakly in E3, and (2) after reactor shutdown, when all the liquid contents have boiled off, as in E3 and weakly in E4.

Inspection of the thermocouple and resistor liquid level probes after the incidents in E2 indicates that the spontaneous explosions that occurred during irradiation periods had their origin at or near the glass fiber spaghetti used as insulation for the wiring, as evidenced by the excessive fraying thereof at certain positions which appeared to be the explosion sites. Although attempts were made to eliminate organic materials of any kind in the construction of the diagnostic instrumentation for the open dewar, it was learned after the experiments that

some of the glass insulation had been coated by the manufacturer with a very thin plastic film. Thus, explosions that occurred during the course of irradiation of the dewars involved regions of the probes which at some time prior to explosions were immersed in the liquid and which had subsequently come out of this liquid during boil-off.

The following is a reasonable explanation of the above-mentioned occurrences. During the course of the irradiation of the dewar and its contents, a certain species is probably formed in the crevices of the glass fiber matrix which, upon exposure to the atmosphere and after lowering of the liquid level in the dewar by liquid boil-off, decomposes or reacts with the organic film violently enough to produce the sounds (pops) heard over the loudspeaker system. Whether the species involved is ozone or some oxide of nitrogen is unknown, although the latter would appear as solid and could deposit out on an object coming out of the liquid during the course of boil-off. If the species involved were ozone, it would probably be a liquid dissolved or totally miscible in the oxygen-containing liquid nitrogen under the conditions of the experiment.

Although Ceramo-insulated wires were used in E3 to replace the Fiberglas insulated wires of E2, explosions occurred in the dewar during the irradiation and resulted in destruction of some of the lower thermocouples. Most of these thermocouples ceased functioning because of severing of the leads higher

up on the probe where the Ceramo-insulated wires were joined to the regular wiring.

There is no doubt that the main spontaneous explosion of an experiment occurred at the end, when all the LN_2 had boiled off, as in E2 and especially in E3. Whether a liquid (other than LN_2) or a solid remained at the bottom of the dewar after complete boil-off of the LN_2 prior to the spontaneous explosion in E2 and E3 (and in E4) is difficult to establish, for the data on temperature measured by the bottom-most thermocouple displayed a general monotonic increase up to the point of explosion, without a marked plateau at any temperature characteristic of the boiling points or melting points of species suspected of being involved in the explosions, such as ozone or oxides of nitrogen.

Explosion can also be induced by specimens, both inorganic and organic, dropped in an irradiated open dewar after reactor shutdown but presumably before all the liquid contents have boiled off, as in E2 and E3, respectively. In both of these cases, a shock-induced explosion cannot be ruled out, especially in E2 when a metal specimen was used.

6.2 Emission Spectroscopy Studies

The spectrographic experiments were conducted in conjunction with the engineering experiments employing a low-dispersion fast spectrograph in E2 and E3 and a high-dispersion, high-aperture spectrograph in E4 and E5. These experiments were

thwarted by a number of conditions, including: the finite time required to set up the spectrographic equipment after reactor shutdown, especially in the early experiments (mainly E2); the high level of background radioactivity after reactor shutdown on the OAT catwalk at the site of recording equipment in some cases; the high level of background stray light of daylight at the end of one of the experiments (E3) that produced a strong explosion; and the weak level of explosion at the end of an experiment (as in E4) when the spectrographic equipment was operating satisfactorily.

It was planned to use a STL Products image-converter camera (ICC) in conjunction with the high-aperture spectrograph to increase the intensity in the spectrograms by a factor approaching 50 in the continuation studies to ensure that even weak explosions would be recorded. Use of this ICC in both the streaking and framing modes in conjunction with the spectrograph would also yield spectral data on temporal variations of the explosions. Use of the ICC (without the spectrograph) in the framing mode would yield information on the spatial and temporal characteristics of the explosions per se at the bottom of the dewar.

6.3 EPR Spectroscopy Studies

EPR spectra of X-irradiated samples of LN_2 containing LOX as an impurity were obtained in situ. These spectra displayed only peaks corresponding to color centers produced

in the quartz dewar which contained the LN_2 -LOX solution. EPR (reference) spectra of unirradiated solid NO_2 in LN_2 and solid NO in LN_2 exhibited resonances; unirradiated solutions of O_2 in LN_2 and O_3 - O_2 in LN_2 showed no resonances. These experiments, however, are not considered conclusive, and further work is indicated.

It is concluded that additional EPR experiments need to be performed on solutions of LN_2 -LOX irradiated to higher doses than in the experiments to date and under such conditions (including irradiation external to the cavity containing the quartz dewar) that the EPR spectrum of color centers of quartz will be suppressed.

6.4 Concluding Remarks

A final word about explosion hazards, i.e., those involving irradiated dewar vessels employing cryogenic fluids other than LN_2 . It has come to the attention of experimenters using closed cryogenic loops and/or regular dewars in a reactor radiation field employing either LHe or LH_2 as the cryogen that explosion problems could arise under two conditions: (1) these systems could develop leaks to the ambient, thus permitting water vapor, oxygen, nitrogen, and other constituents of the ambient to condense and subsequently freeze out on the inside walls of the loops and (2) these constituents of the ambient could also condense on the outside surfaces of cryogenic lines and dewars and collect in pockets thereabouts.

Exposure of these condensed and/or frozen constituents in intense radiation fields of the order of 10^8 r (gamma rays), or higher, and associated integrated neutron fluxes could lead to the same conditions (described in this report) that are characteristic of irradiated cryogenic dewars employing (impure) LN_2 as the cryogenic fluid.

Indeed, at least one such incident has been observed and reported (Ref. 45). Video-tape records of a particular event in the GTR 14 test (part of the SNPO-C studies of radiation effects on NERVA materials and components) show what appears to be a small detonation that originated in a "pool" formed on the surface of the gaseous He shroud, between the LH_2 fill and exhaust lines. Apparently, this pool was formed by air condensing on the uninsulated exhaust line and dripping to the shroud.

Another incident involved minor fires during the NRX-A2 run of 24 September 1964. These fires occurred on a test assembly just above the pressure-vessel closure interface and on the propellant feed line (Ref. 46). Similar incidents of fires have been reported in earlier tests in the series at Jackass Flats, Nevada.

Although a partial study has been conducted on liquid-hydrogen explosions in closed vessels by researchers at the Atomic Energy Research Establishment (AERE), Harwell, England (Ref. 47), it behooves NASA and AEC to conduct additional studies of explosions in irradiated cryogenic vessels to eliminate the explosion hazards, not simply to obviate them.

REFERENCES

1. Romanko, J., Investigations of Explosions in Irradiated Liquid-Nitrogen Vessels, General Dynamics/Fort Worth Report FZP-521, 4 January 1964.
2. Klontz, E. E., United States Atomic Energy Commission Unclassified Report, Number 2267, Purdue University, 1952.
3. Coltman, R. R., Blewitt, T. H., and Noggle, T. S., "Techniques and Equipment Utilized in Low-Temperature Reactor Irradiations," Rev. Sci. Instr. 28 (1957), 375.
4. Sartain, C. C., and Yockey, H. P., "Cryostat for Reactor Irradiation," Rev. Sci. Instr. 29 (1958), 118.
5. McReynolds, A. W., et al., "Neutron Irradiation Effects in Cu and Al at 80°K," Phys. Rev. 98 (1955), 418.
6. Private communication between J. W. Cleland, C. C. Sartain, and H. P. Yockey, Oak Ridge National Laboratory, 1957.
7. Thompson, M. W., and Jefferson-Loveday, D. S., "A cryostat for Reactor Irradiations in Liquid Nitrogen," J. Sci. Instr. 35 (1958), 397.
8. Bangs, L. B., Gregson, T. C., and Manuel, E. H., "Hazards Warning," Nucleonics 17 (1959), 110.
9. Bortels, G., "Cryostat for Reactor Irradiation in Liquid Nitrogen," J. Sci. Instr. 36 (1959), 511.
10. Bochirol, L., Doulat, J., and Weil, L., Cryogenics 44 (1960).
11. Bochirol, L., Doulat, J., and Weil, L., "Principle of a Liquid-Nitrogen Irradiation Device and Its Realization for Use in a Swimming-Pool Type Reactor," Adv. Cryogenic Eng. (Plenum Press, Inc., New York, 1961), Vol. 6, p. 130.
12. "Report of Detonations in Dewars," NERVA Components Irradiation Program; Vol. 1, GTR Test 4, General Dynamics/Fort Worth Report FZK-170-1, 19 July 1963, Appendix B, p. 265.
13. Joy, L. A., Memorandum to W. H. Haase, "Trip Report," 4 June 1963, Aerojet-General Corporation, Azusa, Calif.; Greenhow, W. A., and Suttkus, H. O., Memorandum to C. M. Rice, "May 14 Dewar Incident at GTR," 4 June 1963, Aerojet-General Corporation, Azusa, Calif.

REFERENCES (Cont'd)

14. Kuri, Z., Genshiryoku Kōgyō 7, 12 (1961), 39.
15. Jackson, D., "Explosive Reactions Caused by Irradiated Liquid Nitrogen and Oxygen," AERE Trans. 905, Library Atomic Energy Research Establishment, Harwell, Berkshire, England, September 1962.
16. Brown, D. W., and Wall, L. A., " γ -Irradiation of Liquid and Solid Oxygen," J. Chem. Phys. 65 (1961), 915.
17. Pshezhetsky, S. Ya., "Regularities Observed in the Mechanism and Kinetics of Simple Radiation Induced Reactions," Conference of Academy of Sciences of the U.S.S.R., on the Peaceful Uses of Atomic Energy, Division of Chemical Science, 1-5 July 1955.
18. Pshezhetsky, S. Ya., Myasnikov, I. Ya., and Buneev, N. A., "Formation of Ozone in Liquid Oxygen Under the Action of High-Speed Electrons," Academy of Sciences of the U.S.S.R., Division of Chemical Science, Symposium on Radiation Chemistry, Moscow, 1955.
19. Kircher, J. F., et al., "The Effects of Radiation on Oxygen Designed for Human Consumption," Battelle Memorial Institute Report WADC-TR-59-618, August 1959.
20. Douglas, J. E., Bratt, L. C., and Kinderman, E. M., "Peculiarities of Ozone Formation in Electron Irradiation of Nitrogen-Oxygen Mixtures," J. Chem. Phys. 31 (1959), 1416.
21. Berg, T. G. Owe, Explosions in Pile-Irradiated Liquid Nitrogen, Aerojet-General Corporation (Ordnance Division) Special Report 0716-19 (01) SP, 24 September 1963.
22. Herzberg, G., Molecular Spectra and Molecular Structure; I, Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., New York, 1950).
23. Harteck, P., Reeves, R. R., and Mannella, G., J. Chem. Phys. 29 (1958), 608.
24. Barth, C. A., Research Summary No. 36-9, I, 64, Jet Propulsion Laboratory, Pasadena, 1961.
25. Kaufman, F., Proc. Roy. Soc. (London) A247 (1958), 123.
26. Morgan, J. E., and Schiff, H. I., J. Chem. Phys. 38 (1963), 1495.

REFERENCES (Cont'd)

27. Barth, C. A., "Three Body Reactions," Annales De Geophysique 20, 2 (1964), 182.
28. Bass, A. M., and Broida, H. P., eds., Formation and Trapping of Free Radicals (Academic Press, New York, 1960).
29. Fraenkel, G. K., "Paramagnetic Resonance of Free Radicals," Annals of the New York Academy of Science 67 (1957), 546.
30. Jen, C. K., et al., "Paramagnetic Resonance of Hydrogen Atoms Trapped at Liquid-Helium Temperatures," Phys. Rev. 104 (1956), 846.
31. McConnell, H. M., "Effect of Anisotropic Hyperfine Interactions on Paramagnetic Relaxation in Liquid," J. Chem. Phys. 25 (1955), 709.
32. Perrier, A., and Onnes, H. K., Leiden Communications 139d, 48.
33. Lainé, P., "Recherches sur L'Ozone et ses Propriétés Magnétiques," Ann. de Phys. 3, 11 (1935), 461.
34. Bizette, H., "Sur L'Orientation par de Champs Magnétiques de Quelques Molecules et de Quelques Crystaux," Ann. de Phys. 1, 12 (1946), 233.
35. Lips, E., "Uber die Temperaturabhängigkeit der Suszeptibilität von festem Stickoxyd," Helv. Phys. Acta 8 (1935), 247.
36. Havens, G. G., "The Magnetic Susceptibility of Nitrogen Dioxide," Phys. Rev. 41 (1932), 337.
37. Beringer, R., and Castel, J. G., Jr., "Microwave Magnetic Resonance Spectrum of Oxygen," Phys. Rev. 81 (1951), 82.
38. Beringer, R., and Castle, J. G., Jr., "Magnetic Resonance Absorption in Nitric Oxide," Phys. Rev. 78 (1950), 581.
39. Beringer, R., and Castle, J. G., Jr., "Microwave Magnetic Resonance Absorption in Nitrogen Dioxide," Phys. Rev. 80 (1950), 114.
40. Bird, G. R., Baird, J. C., and Williams, R. B., "Fine Structure in the Electron Spin Resonance Spectra of NO₂ Solutions," J. Chem. Phys. 28 (1958), 738.

REFERENCES (Cont'd)

41. Lin, C. C., "Selected Topics in Microwave Spectroscopy," Doctoral Thesis, Harvard University, 1955.
42. Thorp, C. E., Bibliography of Ozone Technology, Armour Research Foundation of Illinois Institute of Technology, 1955, Vol. II, p. 4.
43. Streng, A. G., and Grosse, A. V., "The Different Solubility Behavior of the Isosteric Liquids CO and N₂ in Liquid Ozone," J. Inorg. Nucl. Chem. 9 (1959), 315.
44. "Oxygen Molecules Dimerize," C and EN (7 September 1964), 42.
45. "Incidents Occurring at the East Irradiation Position (LH₂ Dewar), NERVA Components Irradiation Program; Vol. 4, GTR Test 14, General Dynamics/Fort Worth Report FZK-184-4, 13 November 1964, Appendix C, p. 171.
46. Private communication between E. Miller of SNPO-C and J. Romanko of GD/FW, October 1964.
47. Ward, D. L., Pearce, D. G., and Merrett, D. J., "Liquid-Hydrogen Explosions in Closed Dewars," Adv. Cryogenic Eng. (Plenum Press, Inc., New York, 1964), Vol. 9, p. 390.

DISTRIBUTION

<u>ADDRESSEE</u>	<u>NO. OF COPIES</u>
AFWL, Research and Technical Division Air Force Systems Command Kirtland AFB, New Mexico Attn: WLDN-2 (Maj. R. R. Stewart)	(5)
Headquarters, USAF The Pentagon Washington 25, D. C. Attn: AFRNE-B (Lt. Col. J. T. Burke)	(2)
SNPO-Cleveland Lewis Research Center 21000 Brookpark Road Cleveland 35, Ohio Attn: G. L. Kimball Ernest Miller Paul Ordin J. J. Lombardo	(3) (1) (1) (1)
SNPO-Washington Division of Reactor Development U. S. A. E. C. Germantown, Maryland Attn: J. Morrissey	(2)
National Aeronautics and Space Administration George C. Marshall Space Flight Center Huntsville, Alabama Attn: R-P VE-ME E. C. McKannan	(2)
L. E. Krelovich (Aerojet-General Corporation Representative at GD/FW	(6)
Westinghouse Astronuclear Laboratory P. O. Box 10864 Pittsburgh, Pennsylvania Attn: Dr. S. S. Stein	(6)
Los Alamos Scientific Laboratory Los Alamos, New Mexico Attn: J. Perry E. Brown	(1) (1)

DISTRIBUTION (Cont'd)

<u>ADDRESSEE</u>	<u>NO. OF COPIES</u>
Bendix Corporation Bendix Systems Division Ann Arbor, Michigan Attn: A. G. McLemore Contract Adms.	(4)
SNPO-C Resident Office Aerojet-General Corp Sacramento, Calif. Attn: J. J. Fitts	(1)
Radiation Effects Information Center Battelle Memorial Institute 505 King Avenue Columbus, Ohio	(1)